SOLUBILITY AND SPECIFIC ROTATORY POWER OF CARBOHYDRATES AND CERTAIN ORGANIC ACIDS AND BASES IN PYRIDINE AND OTHER SOLVENTS

BY JOSEPH GERARD HOLTY

The term carbohydrate is applied to a large class of organic substances closely related to each other. The majority of these compounds are soluble in water, though those of the class $(C_6H_{10}O_5)_x$, of which starch and inulin are types are, as a rule, insoluble.

The range of solubility of the carbohydrates in solvents other than water is very limited, only bodies like the sugars have been found to dissolve in liquids such as methyl and ethyl alcohols, acetone and pyridine, and then only to a slight extent.

But little work has been done in determining the solubilities of these compounds in various solvents. At the suggestion of Prof. Kahlenberg, I have investigated the solubility and rotatory power of these substances with the hope of ascertaining the effect of the solvent upon the dissolved substance and the influence of the solvent on the specific rotation of the solute.

In some recent investigations carried on in this laboratory by Prof. Kahlenberg, it was found that cane-sugar was soluble in pyridine. Later investigation by G. M. Wilcox¹ has shown the extent of this solubility and also the influence of the pyridine upon the rotatory power of the cane-sugar. The following work represents a further study of the sugars and other carbohydrates with pyridine as a solvent.

Milk-sugar

The first substance used was milk-sugar. This was one of Schuchardt's preparations and labeled chemically pure. The samples used were first carefully dried at about 100° to expel moisture. The substance then corresponds to $C_{12}H_{22}O_{11} \cdot H_2O$.

The pyridine used was purchased from Kahlbaum. It was

¹ Jour. Phys. Chem., 5, 587 (1901).

first well dried over caustic potash after which it was distilled, and the distillate passing over at 114° – 117° , and corresponding to a density of 0.971 at 20° C., was used in determining the rotatory power.

Two different samples of milk-sugar were taken, the one was boiled in pyridine for several hours and then allowed to cool to room temperature. The other, together with the pyridine, was placed in a large test-tube which was then sealed and fixed to a shaking apparatus immersed in a water-bath maintained at a constant temperature of 26° , and operated by means of an electric motor for about 30 hours. By this method a saturated solution was obtained at that temperature.

The densities of the two solutions were then determined and the angle of rotation observed by means of the Landolt-Lippich polariscope. The specific rotation was calculated according to the formula $[\alpha]_D^t = \frac{\alpha_D^t \times 100}{l \times d \times c}$ where α_D^t = the observed angle at temperature t ; l , the length of the tube in decimeters; c , the number of grams of the solute in 100 grams of the solution; and d , the density of the solution.

It was found upon evaporation of the two solutions that more sugar had dissolved when it had been shaken with the pyridine, than when the mixture had been boiled. An excess of the sugar was used in each case, and the sample that was boiled caked on the bottom of the flask, forming a hard mass. This, no doubt, accounts for the fact of its lesser solubility, for in coalescing the mass would offer less surface to the pyridine than if it were in finer particles.

The sample that was shaken was found to contain 2.18 grams milk-sugar in 100 grams of the solution, while the other contained only 1.38 grams.

The same strength solutions were now made up with water as the solvent.

It has been observed that the specific rotatory power of certain substances in freshly prepared solutions changes gradually, increasing or decreasing until a constant value is obtained. This peculiar change was first noticed by E. O. Erdmann in milk-sugar and later by Tollens and Fischer in other sugars.

Erdmann¹ and Schmoeger² observed, in 1880, that milk-sugar on dehydration changes into a modification, which on resolution shows a gradual increase in rotation. These were known as the α - and β -modifications, but in 1895, Tanret found a third modification, λ , which in solution could be transformed into the β -variety, the latter then being the stable modification, the rotatory power of which is always constant.

The above phenomenon, which is generally spoken of as multi-rotation, is difficult to explain. Some regard the freshly prepared solution as consisting of molecular aggregations which gradually break down into molecules of lower rotation. Others claim that the decrease in rotation may be due to the taking up or splitting off of water, and again it is claimed that it may be due to the existence of different isomeric modifications which, in solution, are transformed into the stable form. The latter view is the most universally accepted one, but as it too is based more or less upon theory, there still remains more work to be done in this connection before we have the true solution of the problem.

To insure complete transformation into the stable variety, the aqueous solutions made, were first boiled, and then allowed to stand for several days. The values obtained as compared with those of the pyridine solution are given in the following table:

Solvent	Percent milk-sugar	Density	$\alpha_D^{26} l = 2\text{cm.}$	$[\alpha]_D^{26}$
Pyridine	2.18	0.981	1.83	42.57
Water	2.18	1.0075	2.26	51.26
Pyridine	1.38	0.9778	1.15	41.39
Water	1.38	1.0043	1.44	52.14

It will be noticed that the values for the rotatory power in aqueous solutions are greater than the corresponding ones in the pyridine solutions; also that the rotatory powers in the pyridine solutions increase with increased concentration. These results

¹ Ber. chem. Ges., Berlin, 13, 1915 (1880).

² Ibid., p. 2180.

show just the reverse of what is true of cane-sugar in pyridine. Values for milk-sugar in aqueous solutions have been obtained by several investigators such as Schmoeger,¹ Parcus and Tollens,² Tanret,³ and Hesse.⁴ Their results agree fairly well. Schmoeger shows that the specific rotatory power of a 2.372 percent solution of milk-sugar is 52.53 at 20°, and that it is independent of the concentration up to 41.536 percent. Exactly the same value was found by Deniges and Bouvans.⁵ The above results agree with those I obtained for about the same percent concentration.

Grape-sugar

The next substance studied was grape-sugar, $C_6H_{12}O_6 \cdot H_2O$. This sugar was a pure sample of Merck's preparation. It was found to be very soluble in pyridine, especially so when the mixture was boiled. The solution obtained by boiling was so dark that one was unable to see through it in the polariscope. Consequently, such a solution could only be used which had been obtained by shaking the sugar with pyridine at room temperature till saturated. Four grams of the grape-sugar were placed together with 50 cc pyridine in a large test-tube which was then sealed and the mixture shaken as in the case of the milk-sugar, in a water-bath at 26° for about 30 hours. At the end of that period, it was found that all the sugar had dissolved. The experiment was then repeated, using 6 grams sugar to 50 cc pyridine and after shaking for 30 hours, it was found that only a little more sugar had been dissolved than in the previous case. This shows that 4 grams of grape-sugar in 50 cc pyridine represents practically a saturated solution at 26°, and corresponds to 7.62 percent. An aqueous solution was now made of the same percent strength. A comparison of results is given below:

¹ Ber. chem. Ges., Berlin, 13, 1918 (1880).

² Liebig's Ann., 257, 170 (1890).

³ Bull. Soc. Chim., Paris (3), 13, 625 (1895).

⁴ Liebig's Ann., 176, 98 (1875).

⁵ Jour. Pharm. Chim. (5), 17, 363; Chem. Centralbl., 603 (1888).

Solvent	Percent grape-sugar	Density	$\alpha_D^{26} l = 2\text{dcm.}$	$[\alpha]_D^{26}$
Pyridine	7.62	1.0050	11.58	75.62
Water	7.62	1.0292	8.22	52.42

The above results show a decided variation from those obtained with milk-sugar solutions. In the latter, the rotatory power was higher for the aqueous solution, whereas in the case of grape-sugar, the pyridine solution yields much the higher values. Values given in Landolt¹ for aqueous solutions of grape-sugar in the stable modification, are:

$[\alpha]_D^{20} = 52.5$ and 52.6 , which agree very closely with those I obtained.

Laevulose

Grape-sugar is more soluble in water than laevulose, but the reverse is true when pyridine is used as the solvent. The laevulose used was purchased from Kahlbaum, and was supposed to be chemically pure. Separate samples containing 4, 7 and 11 grams, respectively, were each placed with 50 cc pyridine in three test-tubes which were drawn off over a flame and shaken for about 30 hours at 26° , in the apparatus heretofore mentioned.

The sugar in each case was totally dissolved which shows an enormous increase in solubility as compared with the grape-sugar. The above solutions represent 7.61, 12.61, and 18.49 percent strength, respectively, the strongest being almost saturated. The solutions were all dark colored and a short tube of 1 decimeter in length had to be used in the polariscope.

The results obtained are tabulated below:

Solvent	Percent strength	Density	$\alpha_D^{26} l = 1\text{dcm.}$	$[\alpha]_D^{26}$
Pyridine	7.60	1.008	— 5.64	—36.82
Water	7.60	1.0298	— 6.83	—87.3
Pyridine	12.61	1.0267	—10.22	—39.47
Water	12.61	1.0505	—11.63	—87.78
Pyridine	18.49	1.0521	—17.67	—45.44
Water	18.49	1.0755	—17.60	—88.51

¹ Landolt's "Optical Rotation of Organic Substances" (translation by Long), p. 261.

It is well known that in aqueous solution laevulose rotates the plane of polarization to the left. This is also true in a pyridine solution, but to a less degree—in other words it approaches nearer to a dextro rotation. The values obtained for the pyridine solution increase quite uniformly with increase in concentration. This is also true of the aqueous solutions, but the variation is very small.

Earlier investigations by Herzfeld¹ and Winter² give specific rotatory powers for aqueous solutions which vary between 70.59 and 71.47 for a 20 percent solution.

Hoenig and Jesser,³ on the other hand, have obtained values very much higher, ranging from 89.42 in a 5 percent solution to 98.47 in a 40 percent solution. The latter investigators claim that the low values obtained by Herzfeld and Winter are due to the formation of dextrans in the conversion of inulin into sugar, which could not have been completely removed by their method of purification with ether and alcohol.

Jungfleisch and Grimbert⁴ give the following values: For a 9.75 percent solution at 20°, $[\alpha]_D = -89.9$ and for a 48.75 percent solution at 40°, $[\alpha]_D = -82.53$.

In looking over the above values obtained by different observers we see a wide variation in results. Their values do not agree with each other, nor do they agree with those I have obtained, with the exception of those derived by Hoenig and Jesser which check fairly well, considering the differences in temperature at which we worked.

Galactose

The galactose used was prepared by H. Trommsdorff. It did not appear to be very pure, which fact was verified by the results obtained in determining its rotatory power in aqueous solutions. It was found to dissolve quite readily in pyridine, but to a much less extent than the laevulose. After shaking a mixture of the sugar in pyridine for about thirty hours, a saturated

¹ Liebig's Ann., 244, 287 (1888).

² Ibid., 244, 300 (1888).

³ Zeit. Rübenzucker Ind. (1888), 1028.

⁴ Comptes rendus, 107, 390 (1888).

solution of 5.45 percent strength was obtained. This percent was determined by evaporating the solution on a paraffin bath. The substance that remained was a thick, dark, amorphous mass, not unlike a stiff syrup. On this account it is difficult to say whether the above result is correct or not, for if the residue was heated too highly, the sugar would be decomposed, while if not heated enough, some of the pyridine would still remain in the residue. The sugar, as soon as it was dissolved, imparted a dark, brownish red color to the solution, and a short tube of 1 decimeter length had to be used in the polariscope. Great care had to be exercised in obtaining concordant readings on the instrument, and many settings had to be made.

The following are the results obtained:

Solvent	Percent sugar	Density	$\alpha_D^{26} l = 1 \text{ cm.}$	$[\alpha]_D^{26}$
Pyridine	5.45	1.0065	3.76	68.49
Water	5.45	1.0196	3.62	65.06

The rotatory power of the two above solutions shows but a slight variation; but, according to results obtained by other investigators, the rotatory power in aqueous solution should be much higher. Rindell¹ gives values for a 10 percent solution as 80.01 at 20° C and as 77.50 at 30° C.

Parcus and Tollens² give $[\alpha]_D^{20} = 80.39$ for a 11.081 per. cent solution. From these values one sees that the specific rotatory power of galactose increases with increased concentration, but decreases very noticeably with increase of temperature.

The low results that I obtained for the aqueous solution are due in part to the weak solutions used and also to the relatively high temperature at which I worked as compared with that at which Parcus and Tollens worked, but the main cause must be attributed to impurities in the sugar.

Mannite

Much work has been done with this substance in aqueous solution and varying results have been obtained. Ordinary

¹ Scheibler's *Neue Zeit. Rübenzucker Ind.*, 4, 170.

² Liebig's *Ann.*, 257, 168 (1890).

mannite dissolved in water was found by Vignon,¹ Muentz and Aubin,² and a few others, to possess no activity, but Bouchardat³ found with a 15 percent solution with a strong sodium light a rotation = -0.25 .

In the aqueous solutions with which I worked, I could find no activity, thus verifying the results obtained by Vignon, Muentz and Aubin.

A very interesting phenomenon was observed in trying to dissolve the mannite in pyridine. At room temperature the substance was very slightly soluble but on boiling, a large amount dissolved. It did not, however, remain in solution very long, but on cooling the greater part of it precipitated out in the form of a bulky spongy mass. It was thought possible that the mannite had formed a solid crystalline addition product with the pyridine, but on further investigation it was found that this was not the case. This was shown by taking a small amount of the spongy mass and carefully drying it on filter-papers. All the pyridine could thus be extracted, and the remaining substance was simply pure mannite.

The solution on cooling to room temperature was very dilute. On evaporation it was found that only 0.47 percent remained in solution, which shows the slight affinity between pyridine and mannite.

The results obtained are given in the following table :

Solvent	Percent mannite	Density	$\alpha_D^{26} l = 2\text{cm.}$	$[\alpha]_D^{26}$
Pyridine	0.47	0.9740	-0.20	-21.71
Water	0.47	1.0014	0.00	00.00

The values obtained for an aqueous solution by Bouchardat show laevo rotation. From this one would suppose that a solution of mannite in pyridine would also show laevo rotation which was found to be true.

¹ Vignon: *Comptes rendus*, 77, 1191 (1873).

² *Ann. Chim. Phys.* (5), 10, 553 (1877).

³ *Comptes rendus*, 80, 120 (1875).

Erythrite

Erythrite is more soluble in pyridine than mannite. On boiling erythrite in pyridine and then allowing the solution to cool, the substance will separate out in form of a large spongy mass like in the case of mannite above described. More of the substance, however, remained in solution than in the former case, but on evaporation the residue remaining was not crystalline, but formed a thick viscous mass of a syrupy consistency. On this account it was very difficult to obtain reliable results representing the percent strength solution that was formed, but by most careful manipulation, a value corresponding to 2.5 percent was obtained. As erythrite is an inactive substance, no further study was made of it.

An attempt was made to determine the solubility and rotatory power of starch and some of the dextrans in pyridine, but it was found that they are all practically insoluble. The same is true of asparagine.

Strychnine, on the other hand, was found to be soluble in pyridine to a slight extent. At high temperatures, the substance was quite soluble, but on cooling to room temperature, it separated out in form of large crystals and the remaining solution on evaporation showed only 1.23 percent strength. The above process is indeed a splendid method to recrystallize the pure base.

An attempt was made to determine the rotatory power at higher temperatures but this was found impossible as the base was continually thrown out of solution, thus blurring the field of vision; hence the results tabulated below are those of a dilute solution obtained at room temperature. Strychnine is insoluble in water and consequently the values obtained for the pyridine solution, can not be compared with those of a corresponding aqueous solution. The results in pyridine solution are as follows:

Solvent	Percent of solute	Density	$\alpha_D^{26} l = 2\text{cm.}$	$[\alpha]_D^{26}$
Pyridine	1.23	0.9772	—4.72	—195.53

To show the effect of other solvents on strychnine, a few results obtained by other investigators¹ where chloroform, ethyl alcohol and amyl alcohol were used, are here tabulated :

Solvent	Percent of solute	$[\alpha]_D^{20}$
CHCl_3	4.00	—130.0
"	2.25	—137.7
"	1.50	—140.7
$\text{C}_2\text{H}_5\text{OH}$	0.91	—128.0
$\text{C}_5\text{H}_{11}\text{OH}$	0.53	—235.0

The above figures show, in each case, a strong laevo-rotatory power and also a low solubility in the different solvents. The rotation varies widely with each solvent, and in the case of chloroform, with the concentration.

In connection with the above work on the carbohydrates and a few bases, it was thought of interest to see what influence pyridine would have on some of the active organic acids.

Malic acid

Concentrated aqueous solutions of malic acid are dextro-rotatory, which rotation, however, decreases with elevation of temperature; dilute solutions are laevo-rotatory, which property increases with increase of temperature.

In pyridine, malic acid is readily soluble. Two solutions were made at room temperature, corresponding to 7.62 percent and 14.16 percent malic acid, respectively. Aqueous solutions of the same strength were made, and a comparison of results obtained follows :

Solvent	Percent malic acid	Density	$\alpha_D^{26} l = 2\text{cm.}$	$[\alpha]_D^{26}$
Pyridine	7.62	0.9742	—4.00	—26.92
Water	7.62	0.9996	—0.36	— 2.07
Pyridine	14.16	0.9998	—7.15	—50.06
Water	14.16	1.0256	—0.53	— 1.81

¹ Oudemans: Liebig's Ann., 166, 76 (1873).

One sees from these values that pyridine has a marked influence in lowering the rotatory power of malic acid. It is also of interest to notice that the lowering is almost directly proportional to the concentration of the solution. In aqueous solution, the reverse order is true. Here the highest laevo-rotatory power is obtained in the most dilute solution, which fact is corroborated by results obtained by other investigators.

G. H. Schneider¹ gives for a 8.32 percent aqueous solution of malic acid, $[\alpha]_D^{20} = -2.30$, and for a 14.35 percent solution, $[\alpha]_D^{20} = -1.73$, which results agree quite closely with those I obtained.

Tartaric acid

Tartaric acid is quite soluble in pyridine, but to a lesser extent than malic acid. A fairly concentrated solution can be obtained, but this, on shaking or heating, will precipitate out a white, spongy mass, the whole solution becoming a sort of quasi-solid. This mass is undoubtedly pyridine tartrate.

Pyridine is a fairly strong base and behaves as such toward acids, forming salts. In the work with the above acids then, we are dealing with the pyridine salts of the organic acids used dissolved in an excess of the solvent, and the results obtained must be interpreted accordingly.

The solubility and rotatory power of tartaric acid in pyridine has been determined by Richard Pribram,² whose results can be found in the reference given below.

While working with tartaric acid in pyridine it was thought of interest to study one of its esters and the substance selected was di-*n*-propyl tartrate. The latter substance is a thick, oily liquid, boiling-point 303° at 760 mm. The sample used was considered to be of a high degree of purity, which fact was verified by the determination of its specific gravity and also its specific rotatory power. Upon investigation it was found that the propyl tartrate dissolved in pyridine in all proportions and hence no trouble was encountered in studying its rotatory power in pyridine at different concentrations.

¹ Liebig's Ann., 207, 257 (1881).

² Ber. chem. Ges., Berlin, 22, 6 (1889).

The following table gives the values obtained for solutions containing from 100 to 1/8 percent propyl tartrate in pyridine:

Percent propyl tartrate	Density	α	$[\alpha]_D$
100	1.1302	28.78	12.73
95	1.1220	35.94	16.86
90	1.1177	40.75	20.26
75	1.0996	48.09	31.04
50	1.0588	43.06	40.66
25	1.0163	24.27	47.76
20	1.0064	19.20	47.69
15	0.9999	14.39	47.99
10	0.9904	9.67	48.82
5	0.9822	4.81	48.99
2	0.9771	1.96	50.15
0.5	0.9747	0.51	51.81
0.25	0.9743	0.26	50.29
0.125	0.9740	0.12	50.10

The curve obtained by using the specific rotation as ordinates and the proportion of propyl tartrate in the solution as abscissas is represented in Fig. 1.

Fig. 1

From this curve we see that the specific rotatory power decreases with increased dilution until a maximum is reached, which point is only obtained when we have a solution containing less than one-half percent propyl tartrate. From this point the drop must be quite sudden, for the pyridine itself is inactive.

The question as to whether the solubility of a substance in a solvent depends upon the size of the solid particles used or

not, has received some attention of late. G. A. Hulett,¹ in his work upon the "Relations between Surface Tension and Solubility," has come to the conclusion that the concentration of a solution varies with the size of the solid particles.

It was thought of interest in this connection to see if this was true in the case of cane-sugar in pyridine. A sample of pure rock candy was obtained, ground in a mortar and passed through a series of six sieves representing 6, 12, 40, 80, 100 and 120 meshes per square inch respectively. The different sized samples were then dried for about half an hour at about 100° to expel the moisture and then each placed in a flask containing pyridine and boiled on a paraffine bath for about eight hours. The rotatory power of the different solutions was then determined, but the results obtained were of no special value, for they indicated just the reverse from what we expected. The solutions formed from the coarsest grains were the most concentrated, which undoubtedly was due to the fact that the finest particles on boiling caked more than the coarser ones, thus offering less surface to the action of the solvent. As this method proved impracticable, it was deemed best to proceed, as heretofore explained, by shaking the mixtures of sugar and pyridine at room temperature. The shaking was continued for about forty hours at 26° to insure complete saturation, and the rotatory power was then observed as before. The results obtained showed no difference in the concentration of the solutions, which fact proves that Hulett's theory does not hold good for cane-sugar in pyridine at least.

By the above method I was able to obtain a 6.45 percent solution of sugar in pyridine, a value slightly higher than 6.25 percent, the value obtained by G. M. Wilcox.² According to the latter, the rotatory power of cane-sugar in pyridine decreases with increased concentration. This was corroborated by the results I obtained.

Wilcox gives for a 4 percent solution, $[\alpha]_D^{25} = 84.7$, and

¹ Zeit. phys. Chem., 37, 385 (1901).

² Jour. Phys. Chem., 5, 587 (1901).

for a 6.25 percent solution, $[\alpha]_D^{25} = 83.6$. For the 6.45 percent solution, I obtained the value $[\alpha]_D^{26} = 82.97$, which agrees very closely with the results of Wilcox.

It is a well-known fact that the rotatory power of a substance is dependent upon the nature of the solvent used. If the same amount of an active substance is dissolved in inactive liquids of different nature, the rotatory power assumes different values, depending on the action of the solvent on the dissolved substance. The specific rotation of the substance dissolved may be increased or decreased. Cane-sugar which shows but slight deviations in rotation with reference to concentration and temperature in aqueous solutions shows marked deviation when dissolved in different solvents. Tollens¹ gives the following values for cane-sugar in water, methyl and ethyl alcohols and acetone :

10 parts sugar, 90 parts water,	- - - -	$[\alpha]_D = 66.67$
10 parts sugar, 23 parts water,	67 parts ethyl alcohol,	" = 66.83
	acetone,	" = 67.40
	methyl alcohol,	" = 68.63

By the introduction of various amounts of benzene, carbon bisulphide, acetone, nitro-benzene and chloroform into separate samples of the saturated solution of sugar in pyridine, I obtained the following results :

6.45 grams sugar, 93.55 grams pyridine	$[\alpha]_D^{26} = 82.97$
addition of 24.12 grams of benzene	" = 81.59
addition of 34.46 grams of carbon bisulphide	" = 79.59
addition of 31.42 grams of acetone	" = 80.92
addition of 51.10 grams of nitro-benzene	" = 87.11
addition of 18.14 grams of chloroform	" = 88.19

From these results we see that the addition of each different solvent causes a marked variation in the rotatory power of the solution. The presence of carbon bisulphide, acetone and benzene tend to decrease the rotatory power, whereas nitro-benzene and chloroform increase it to a marked extent. Before a satisfactory explanation of these phenomena can be given,

¹ Ber. chem. Ges., Berlin, 13, 2303 (1080).

there still remains more work to be done on the nature of solutions.

It seems difficult, however, to explain the observed facts without the assumption of combination of the active substance with these ingredients which so markedly effect the rotatory power.

Summary

The results given in the foregoing pages may be briefly summarized as follows:

The order of solubility of the investigated substances in pyridine, beginning with the most soluble is as follows, the figures indicating parts by weight contained in 100 parts by weight of solution:

Laevulose,	-	-	-	-	18.49
Malic acid,	-	-	-	-	14.60
Grape-sugar,	-	-	-	-	7.62
Cane-sugar,	-	-	-	-	6.45
Galactose,	-	-	-	-	5.45
Erythrite,	-	-	-	-	2.50
Milk-sugar,	-	-	-	-	2.18
Strychnine,	-	-	-	-	1.23
Mannite,	-	-	-	-	0.47

Propyl tartrate not being recorded in the above list stands by itself, it being soluble in all proportions.

It is interesting to note the very great difference in solubility exhibited by malic acid and strychnine. This is hardly surprising, considering the basic and acidic characters of the two substances and the basic nature of the solvent employed.

Saturated solutions in pyridine of cane-sugar, grape-sugar, laevulose and galactose show a greater specific rotatory power than solutions of the same concentration in water. The greatest difference appears in the case of laevulose, while for galactose the difference is very slight. The differences in the case of cane-sugar and grape-sugar are intermediate between the other two mentioned above.

On the other hand, the substances which show a less specific rotatory power in concentrated solutions in pyridine as compared with solutions of same concentration in water are: milk-sugar, mannite, strychnine and malic acid. Of these, the greatest difference appears in the case of malic acid, the difference decreasing with strychnine, mannite and milk-sugar in the order named.

In conclusion, I wish to express my thanks to Prof. Kahlenberg, who has offered so many suggestions and kindly assisted me in the above work.

*Laboratory of Physical Chemistry,
University of Wisconsin, Madison, Wis.
June, 1905.*