There may be some question of the accuracy of results obtained by this method, because of the possible presence of other reducing substances, and the fact that the error is multiplied by such a large factor; but it seems fair, at least to consider that they represent proximate maximum values. The difference between the values for "Total carbohydrates extracted by water and 1% HCl" and for "total carbohydrates by difference" would indicate the presence of hemicellulose-like substances. Moreover, the structure of the artichoke makes this seems the more probable.

It has been shown[1] that the human digestive tract secretes no enzymes capable of digesting either hemicellulose or inulin, and there is some evidence[2] that inulin is not utilized by the animal body.

There is some reason to doubt, therefore, whether the larger part of the carbohydrate of the globe artichoke is in a form that can be utilized by the human organism.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 336.]

THE SPECIFIC ROTATION OF FRUCTOSE.

BY WARREN C. VOSBURGH.[3]

Received May 21, 1920.

In the course of an investigation of the determination of the amount of sucrose and invert sugar in their mixtures it was found that considerable disagreement exists in the literature as to the specific rotation of fructose. For example the specific rotation for a concentration of 5 g. per 100 cc. (4.93% by weight) according to several observers is as follows.

$[\alpha]_D^{20}$	$[\alpha]_D^{25}$	
89.64	86.84	Jungfleisch and Grimbert[a]
89.40	86.04	Honig and Jesser[b]
92.45	89.65[c]	Ost[d]
91.0[e]	88.0	Nelson and Beegle[f]

[a] Jungfleisch and Grimbert, $[\alpha]_D^t = -(101.38 - 0.56\,t + 0.108\,(c - 10))$, *Compt. rend.*, **107**, 390 (1888).

[b] Honig and Jesser, $[\alpha]_D^t = -(88.13 - 0.2385\,p + 0.6714\,(t - 20))$, *J. Deut. Zucker-ind.*, **38**, 1028 (1888).

[c] Using the temperature coefficient of Jungfleisch and Grimbert.

[d] Ost, $[\alpha]_D^{20} = -(91.90 + 0.111\,p)$, *Ber.*, **24**, 1636 (1891).

[e] Interpolated between 15° and 25°.

[f] Nelson and Beegle, THIS JOURNAL, **41**, 559 (1919).

[1] Cf. M. D. Swartz, *Trans. Conn. Acad. Sci.*, **16**, 297 (1911), for a review of this literature.

[2] R. Okey, *J. Biol. Chem.*, **39**, 149 (1919).

[3] National Research Fellow.

There is disagreement also as to the temperature coefficient of the specific rotation. In order, therefore, to obtain accurate values of the specific rotation for different concentrations at 25° which were needed in the above mentioned investigation, it was necessary to make several measurements for various concentrations.

In this investigation it has been found that:

(1) The specific rotation of fructose at 25° can be expressed, in terms of the per cent. by weight, p, and the concentration in grams per 100 cc., c, respectively, by means of the equations,

$$[\alpha]_D^{25} = -(88.50 + 0.145\, p) \qquad \text{(I)}$$

$$[\alpha]_D^{25} = -(88.50 + 0.150\, c - 0.00086\, c^2). \qquad \text{(II)}$$

These equations are based on experimental results for the range $p = 2.6$ to $p = 18.6$ and $c = 2.6$ to $c = 20$.

(2) The temperature coefficient of the specific rotation is a function of the concentration.

(3) The relation between specific rotation and temperature for temperatures between 15° and 37° can be expressed as

$$[\alpha]_D^{t} = [\alpha]_D^{25} + (0.566 + 0.0028\, c)\,(t - 25). \qquad \text{(III)}$$

(4) The values for the specific rotation found in this investigation are from 2° to 3° higher than those calculated from the formulas of Jungfleisch and Grimbert, and Honig and Jesser.

(5) The formula of Ost gives values higher at concentrations below 10% and lower above 10% than the specific rotations found in this investigation.

(6) The equation $[\alpha]_D^{20} = -(91.50 + 0.133\, p)$ expresses Ost's results better than the equation given by him.

(7) Ost's experimental values for the specific rotation for concentrations up to 10% are in good agreement with the values calculated from Equations I and III of this investigation.

Purification of the Fructose.—Five different lots of fructose were purified by recrystallization from strong acetic acid solution as recommended by Hudson and Dale[1] for the purification of glucose. The purified fructose was dried for several hours at 40° *in vacuo* over conc. sulfuric acid and preserved in glass-stoppered bottles in a desiccator over conc. sulfuric acid.

Preparations 1 and 2 resulted from recrystallization of some fructose previously purified in this laboratory by Nelson and Beegle.[2]

Preparation 3 was obtained by 2 recrystallizations of some commercial fructose.

Preparation 4 was the result of a third recrystallization of a portion of

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[1] Hudson and Dale, THIS JOURNAL, 39, 320 (1917).

[2] *Loc. cit.*

Preparation 3. The good agreement of the specific rotation of this preparation with that of the other preparations is good evidence of the purity of the material used in this investigation.

Preparation 5 was the result of 3 recrystallizations of fructose similar to that used in Preparation 3.

Procedure.—The required amount of fructose was weighed, dissolved in distilled water and made up to 100 cc. at the temperature of measurement in a calibrated volumetric flask. The solution was then weighed in order that the per cent. by weight could be calculated in addition to the volume concentration. In some of the experiments of Tables III and IV the solution was made up at one temperature and the rotation measured at another. In that case the density was determined at the temperature in question as well as at the temperature at which the solution was made up to volume and the required concentration calculated. All weights were reduced to a vacuum in the calculations.

All solutions were allowed to stand until mutarotation was complete.[1] The angular rotation of at least 2 samples of each solution was then measured and the mean value taken as the angular rotation of the solution.

For the measurement of the angular rotation a Schmidt and Haensch polarimeter sensitive to 0.01° was used. The solution being measured was maintained accurately at the desired temperature by the use of the thermostat described by Nelson and Beegle.[2] The polariscope tubes were measured and found to be 199.94 mm. and 200.39 mm. in length respectively and all observed angular rotations given were corrected to apply to a 200 mm. tube. At least 4 polariscope settings were made for each sample in the manner recommended by Browne.[3]

Two different light sources were used in the polariscopic measurements. Most of the measurements were made with the use of a sodium lamp, the light from which was not purified. The other source of light, which was used in the experiments of Table V, was a mercury-vapor lamp the light from which was purified by passing through a Wratten No. 74 filter, giving light of wave length $\lambda = 546\mu\mu$.

The Specific Rotation at 25°.—Determinations were made as given in Table I using sodium light. The first column gives the weight of fructose in 100 cc. of solution. The second gives the density as determined by weighing the 100 cc. of solution. The third column gives the composition in per cent. by weight calculated by dividing the weight per 100 cc. by

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[1] A calculation from the results of Nelson and Beegle, *loc. cit.*, shows that the mutarotation of pure β-fructose would be 99.9% complete after 84 minutes at 15° or after 35 minutes at 25° at the hydrogen ion concentration giving minimum velocity.

[2] *Loc. cit.*

[3] Browne, "A Handbook of Sugar Analysis," 1912, p. 106.

the density of the solution. The figures in the fourth column refer to the particular preparation of fructose used. The fifth column gives the angular rotation, and the sixth the specific rotations calculated from the observed rotations and the volume concentrations.

TABLE I.

Specific Rotation of Fructose at 25°.

Conc. in g. /100cc.	Density.	% by wt.	Fructose.	Observed rotation.	Specific rotation.
2.632	1.0073	2.61	1	—4.68	—88.91
2.632	1.0071	2.61	2	—4.67	—88.72
2.632	1.0062	2.62	3	—4.69	—89.09
5.003	1.0164	4.92	1	—8.94	—89.35
5.003	1.0160	4.92	2	—8.91	—89.05
5.003	1.0160	4.92	3	—8.91	—89.05
5.265	1.0170	5.18	1	—9.42	—89.46
5.265	1.0173	5.18	2	—9.39	—89.17
7.900	..	...	1	—14.16	—89.62
7.900	1.0268	7.69	3	—14.16	—89.62
10.006	1.0348	9.67	1	—17.99	—89.90
10.006	1.0349	9.67	2	—17.98	—89.85
10.006	1.0350	9.67	4	—17.99	—89.90
15.009	1.0539	14.24	3	—27.18	—90.55
15.009	..	...	3	—27.21	—90.65
20.012	1.0729	18.65	4	—36.48	—91.14

Ost[1] and Honig and Jesser[1] have expressed the specific rotation of fructose as a linear function of the per cent. fructose by weight, while Jungfleisch and Grimbert[1] express it as a linear function of the volume concentration. However if the per cent. by weight is plotted against the volume concentration a curve is obtained which is not quite a straight line showing that there is not a direct proportionality between the two. specific rotation therefore cannot be a linear function of both. When the specific rotation was plotted against both per cent. and concentration it was found that in the former case the observed points lay more nearly on a straight line than in the latter. The relation between specific rotation and per cent. fructose, p, is shown graphically in Fig. 1, the values for the specific rotation being the mean values given in Table II. The equation of the straight line in Fig. 1 is

$$[\alpha]_D^{25} = -(88.50 + 0.145\,p). \tag{I}$$

As it is often more convenient to deal with concentrations by volume an equation expressing the specific rotation as a function of the concentration, c, in g. per 100 cc. was derived by the method of least squares, from the values in Table II.

$$[\alpha]_D^{25} = -(88.50 + 0.150\,c - 0.00086\,c^2). \tag{II}$$

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[1] *Loc. cit.*

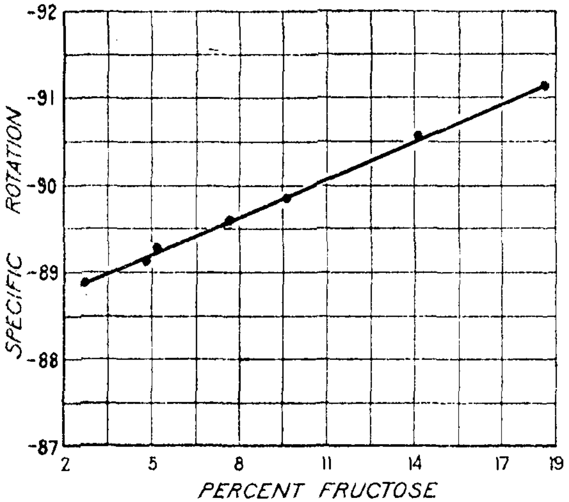

Fig. 1.—Variation of the specific rotation of fructose with concentration.

These equations obviously have not been experimentally verified outside the limits $p = 2.6$ to $p = 18.6$ in I, and $c = 2.6$ to $c = 20$ in II.

Table II gives a summary of the mean values of the observed specific rotations as given in Table I, together with values calculated by means of Equations I and II for the same concentrations. The equations are shown to give values which agree very closely with the experimental values.

Table II.

Comparison of the Observed Specific Rotation with that Calculated from Equations I and II.

Conc. in g. /100 cc.	% by wt.	Specific rotation at 25° Observed.	Calc. I.	Calc. II.
2.632	2.61	—88.91	—88.88	—88.89
5.003	4.92	—89.15	—89.21	—89.23
5.265	5.18	—89.32	—89.25	—89.27
7.900	7.69	—89.62	—89.62	—89.63
10.006	9.67	—89.89	—89.90	—89.91
15.009	14.24	—90.60	—90.56	—90.56
20.012	18.65	—91.14	—91.20	—91.16

Temperature Coefficient.—There is considerable disagreement also as to the temperature coefficient of the specific rotation of fructose. Jungfleisch and Grimbert[1] give 0.56° as the temperature coefficient while Honig and Jesser[1] found 0.671° for a 9% solution and 0.692° for a 23.5% solution. Nelson and Beegle[1] found a difference of 6.0° in the specific rotations at 15° and 25° and a difference of 7.0° between 25° and 37°. Assuming a constant coefficient over this range their temperature coefficient is 0.59° per degree centigrade, determined for a concentration of 5 g. per 100 cc.

The temperature coefficient was therefore determined by means of the experiments given in Table III. The temperature was maintained at the figures given within ±0.05°. The solutions were made up at the

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[1] *Loc. cit.*

temperatures at which the measurement was to be made except in case of the measurements at 0°, 15° and 20° in which case the densities at the 2 temperatures were determined and the concentration at the temperature of measurement calculated. In all cases care was taken to allow the solution to stand at the temperature of measurement long enough for mutarotation to be completed before measurements were made.

TABLE III.

Specific Rotation of Fructose at Various Temperatures.

Temperature. °C	g. per. 100 cc.	Observed rotation.	Specific rotation. Observed.	Specific rotation. Calculated.[a]	Difference.
0.2	5.038	—10.34	—102.63	—103.65	—1.02
15.3	5.039	— 9.55	— 94.76	— 94.78	—0.02
25.0	5.003	— 8.92	— 89.15	..	..
30.0	5.003	— 8.62	— 86.15	— 86.25	—0.10
37.1	5.003	— 8.24	— 82.35	— 82.13	+0.20
0.2	10.080	—20.89	—103.63	—104.75	—1.12
15.0	10.080	—19.32	— 95.83	— 95.84	+0.01
20.0	10.028	—18.64	— 92.94	— 92.87	+0.07
25.0	10.006	—17.99	— 89.90	..	..
30.0	10.006	—17.39	— 86.90	— 86.93	—0.03
37.1	10.006	—16.57	— 82.80	— 82.73	+0.07

$[\alpha]^t_D = [\alpha]^{25}_D + (0.566 + 0.0028\,c)(t - 25)$.

When the observed specific rotations are plotted against temperature between 15° and 37° for both concentrations, as in Fig. 2, two straight lines are obtained which are not parallel, showing that the temperature coefficient does not vary with temperature over this range but that it does vary with concentration. The slope of the specific rotation-temperature line for a concentration of 5 g. per 100 cc., Curve II, is $d[\alpha_5]^t_D/dt = 0.580$ and for a concentration of 10 g. per 100 cc., Curve I, $d[\alpha_{10}]^t_D/dt = 0.594$. Assuming the difference in slopes to be proportional to the difference in concentrations[1] the difference for one g. difference in concentration is $^1/_5$ (0.594-0.580) or 0.0028 and the slope for zero concentration is

$$d[\alpha_0]^t_D/dt = 0.580 - (5 \times 0.0028) = 0.566.$$

Therefore for any concentration

$$d[\alpha]^t_D/dt = (0.566 + 0.0028\,c).$$

Integrating,

$$[\alpha]^t_D = (0.566 + 0.0028\,c)\,t + C.$$

When $t = 25°$, $[\alpha]^t_D = [\alpha]^{25}_D$, and $C = [\alpha]^{25}_D - 25\,(0.566 + 0.0028\,c)$.

Therefore $$[\alpha]^t_D = [\alpha]^{25}_D + (0.566 + 0.0028\,c)\,(t - 25). \qquad \text{(III)}$$

The values for the specific rotation under the conditions of the experi-

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[1] This assumption is sufficient for the purpose if only roughly true since the correction to the temperature coefficient is small and a large error in the correction would make little difference in the result.

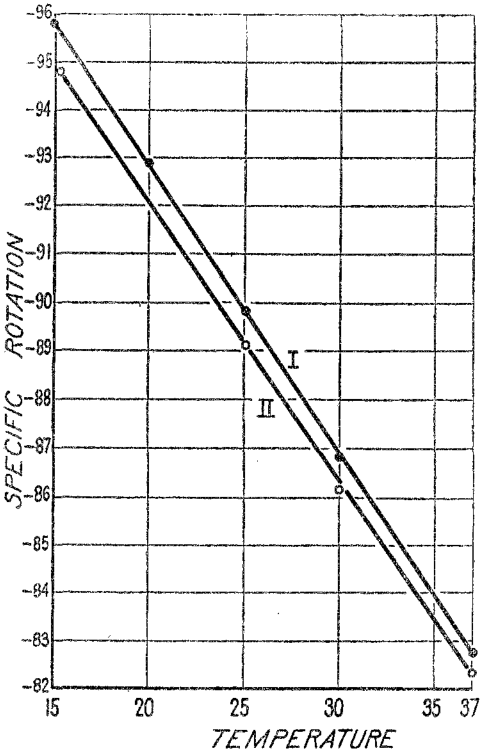

FIG. 2.—Variation of the specific rotation of fructose with temperature. Curve I, concentration of fructose, 10 g. per 100 cc. Curve II, concentration of fructose, 5 g. per 100 cc.

ments of Table III were calculated by means of this equation and are given in Table III. The maximum difference between observed and calculated, except at 0.2° is 0.2° or 2.4 parts per thousand, corresponding to an error in the observed rotation of 0.02°.

The equation evidently does not hold at 0.2° and consequently cannot be depended upon much below 15°.

Results of Other Observers.—Comparison of the specific rotation for a concentration of 5 g. per 100 cc. as given in Table II with the values given by the formulas of Jungfleisch and Grimbert, and Honig and Jesser, as given above, shows that the latter values are 2° to 3° too low, as Ost has pointed out.[1]

The specific rotation as given by the formula of Ost is too high for concentrations up to about 10% and too low above this point as compared with the results of this investigation, as the following figures show.

% Fructose.	5.	10.	15.	20.
$[\alpha]_D^{20}$ Ost	92.45	93.01	93.57	94.12
$[\alpha]_D^{20}$ I and III	92.13	92.93	93.73	94.53

The specific rotation increases too slowly with concentration in the equation proposed by Ost and the value for zero concentration is too high if the results of this investigation are correct. An examination of Ost's experimental results shows that they can be expressed as well or better by the equation $[\alpha]_D^{20} = -(91.50 + 0.133\,p)$. Moreover values calculated from above Equations I and III agree with Ost's experimental values up to the 10% solution, and the values for 5 and 10% given by Equations I and III are closer to the experimental values than those calculated from either of the other equations. Table IV demonstrates these facts. The first 3 columns are taken from Ost's paper and the last 3 were calculated by the author.

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[1] *Loc. cit.*

TABLE IV.

Ost's Observed Values for the Specific Rotation of Fructose Compared with Values Calculated by Various Empirical Formulas.

% Fructose.	Observed rotation.	Specific rotation			
		Observed.	Calc. A (1).	Calc. B (2).	Calc. C (3).
1.0100	—3.67	—90.64	—92.01	—91.63	—91.50
1.0324	—3.74	—90.36	—92.01	—91.64	—91.50
1.9949	—7.37	—91.79	—92.12	—91.77	—91.65
2.0263	—7.49	—91.84	—92.13	—91.77	—91.65
4.9395	—18.56	—92.30	—92.45	—92.16	—92.12
4.9575	—18.59	—92.11	—92.45	—92.16	—92.12
4.9710	—18.64	—92.10	—92.45	—92.16	—92.12
7.8051	—29.86	—92.90	—92.77	—92.54	—92.57
8.9724	—34.50	—92.96	—92.90	—92.69	—92.76
9.8195	—37.88	—92.92	—92.99	—92.81	—92.89
10.5198	—40.72	—93.00	—93.07	—92.90	—93.00
18.5161	—74.61	—93.73	—93.96	—93.96	—94.28
20.2638	—82.47	—94.03	—94.15	—94.20	—94.56
29.7995	—128.23	—95.51	—95.20	—95.46	...
30.1157	—129.60	—95.39	—95.24	—95.50	...

(1) $[\alpha]_D^{20} = -(91.90 + 0.111\,p)$
(2) $[\alpha]_D^{20} = -(91.50 + 0.133\,p)$
(3) $[\alpha]_D^{20} = -(88.50 + 0.145\,p) + (0.566 + 0.0028\,c)(20-25)$

Ling, Eynon and Lane[1] find $[\alpha]_D^{18.5} = -93.83$ when $c = 10$ for some fructose which they describe as of high purity. Calculation by means of the above Equations II and III gives $[\alpha]_D^{18.5} = -93.77$, agreeing with this experimental value within one part in a thousand.

Specific Rotation Measured with the Yellow-Green Line of Incandescent Mercury Vapor.—After most of the above determinations were completed a mercury vapor lamp was installed in this laboratory for use in polariscopic measurements, and a determination was made of the ratio of the specific rotations for the unpurified sodium light as used in the measurements above and the line $\lambda = 546\mu\mu$ obtained by passing the light from the mercury vapor lamp through a Wratten No. 74 filter. For this purpose the rotation of the solutions used for the determination of the temperature coefficient was determined by the use of mercury light as well as sodium light, the light source being changed during the measurements without changing the solutions in the polariscope tubes. The ratio of the rotation using mercury light to that using sodium light was calculated and is the same as the ratio of the corresponding specific rotations. The specific rotation of fructose with the line $\lambda = 546\mu\mu$ as the light source can therefore be calculated from the above results by multiplying by the proper factor. The experimental results and factors to be so used are given in Table V.

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[1] Ling, Eynon and Lane, *J. Soc. Chem. Ind.*, 28, 730 (1909).

TABLE V.

Determination of the Ratio $\frac{[\alpha]^t_{\lambda = 546\mu\mu}}{[\alpha]^t_D}$ for Fructosee.

Temperature ° C.	Conc. in g. /100 cc.	Observed rotation. D line.	Observed rotation. $\lambda = 546\ \mu\mu$.	$\frac{[\alpha]^t_D}{[\alpha]^\lambda_{t = 546\mu\mu}}$.	$\frac{[\alpha]^t_{\lambda = 546\ \mu\mu}}{[\alpha]^t_D}$.	Variation from mean.
0.2	5.038	—10.34	—12.21	0.8468	1.1809	±0.0000
15.3	5.039	— 9.55	—11.27	0.8474	1.1801	—0.0008
25.0	5.003	— 8.92	—10.55	0.8455	1.1828	+0.0019
30.0	5.003	— 8.62	—10.20	0.8451	1.1833	+0.0022
37.1	5.003	— 8.24	— 9.76	0.8443	1.1845	+0.0036
0.2	10.080	—20.89	—24.63	0.8482	1.1790	—0.0019
15.0	10.080	—19.32	—22.75	0.8492	1.1775	—0.0025
25.0	10.006	—17.99	—21.27	0.8458	1.1823	+0.0014
30.0	10.006	—17.39	—20.51	0.8479	1.1794	—0.0015
37.1	10.006	—16.57	—19.55	0.8476	1.1799	—0.0010
25.0	15.0	—27.09	—32.00	0.8466	1.1812	+0.0003
25.0	20.0	—36.34	—42.87	0.8477	1.1797	—0.0012

The ratios of the specific rotations using mercury and sodium lights respectively seem to vary with temperature at a concentration of 5 g. per 100 cc. becoming slightly larger as the temperature increases, but in the case of 10 g. per 100 cc. the ratio seems to be constant over the temperature range considered. If the values at 25° for the different concentrations are considered a regular variation with concentration amounting to less than 3 parts per thousand is noticed. However these variations are hardly larger than the experimental errors and for most purposes the mean value of the ratio, namely 1.1809, or its reciprocal, 0.8467, can be used. The average variation from the mean in the above figures is about one part in a thousand while the extreme variation is 3 parts per thousand.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY.]

RESEARCHES ON AMINES. VIII.[1] THE PREPARATION OF AMINO-ACETANILIDE.

BY ARTHUR J. HILL AND ERWIN B. KELSEY.

Received May 24, 1920.

In order to develop certain phases of an extended research on thiocyanates and isothiocyanates, now in progress in the Sheffield Laboratory, it became necessary to obtain representatives of a series of amines of the general formula $RNHCOCH_2NH_2$, of which amino-acetanilide, $C_6H_5NHCOCH_2NH_2$, is the prototype. Our attention was first turned to this latter compound, since it was evident that the principles underlying a successful method for its preparation would apply directly to the

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[1] Paper VII, *J. Ind. Eng. Chem.*, 12, 636 (1920).