(a) isomeric alkyl tetrahydrofuryl carbinols, (b) isomeric alkyl-*n*-propyl 1,2 glycols, (c) alkyl 1,5-glycols, (d) alkyl butyl carbinols.

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[CONTRIBUTION FROM THE NEW YORK SUGAR TRADE LABORATORY]

THE SPECIFIC ROTATION OF INVERT SUGAR AND THE CLERGET DIVISOR

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During an investigation at present in progress in this Laboratory and involving the analysis of sugar mixtures, we had occasion to refer to Vosburgh's paper on the same subject.[1] This author showed that, contrary to the opinion held generally,[2] the specific rotation of invert sugar at a given concentration is not the sum of the specific rotations of glucose and fructose at their partial concentrations, but one-half of the sum of the specific rotations of the two sugars at the total sugar concentration. Browne has already pointed out the significance of Vosburgh's conclusions for practical sugar analysis.[3]

Vosburgh did not formulate from his results an equation for the specific rotation of invert sugar, nor did he make any comparisons with the values obtained by former investigators. Since the specific rotation of invert sugar is not only an important physical constant, but also forms the basis of the Clerget divisor, it was decided to make use of Vosburgh's data for the purpose just mentioned.

If we reduce Vosburgh's equation for the specific rotation of fructose,[4] which he established for the temperature of 25°, to the standard temperature of 20°, by using his temperature correction formula,[4] we obtain

$$[\alpha]^{20}_{\mathrm{D}} = -(91.33 + 0.164\,c - 0.00086\,c^2) \qquad (1)$$

By combining this equation, according to Vosburgh's rule, with that for the specific rotation of glucose, given by Tollens[5] and recalculated by Browne[6] to the basis of c instead of p,

$$[\alpha]^{20}_{\mathrm{D}} = 52.50 + 0.0227\,c + 0.00022\,c^2 \qquad (2)$$

we get the following equation for invert sugar, valid between 2.6 and 20 g. per 100 cc.

$$[\alpha]^{20}_{\mathrm{D}} = -(19.415 + 0.07065\,c - 0.00054\,c^2) \qquad (3)$$

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[1] Vosburgh, THIS JOURNAL, **43**, 219 (1921).

[2] Compare Landolt, "Das optische Drehungsvermögen," Friedrich Vieweg und Sohn, Braunschweig, **1898**, 2d ed., pp. 214–216.

[3] Browne, *Louisiana Planter*, **67**, 44 (1921).

[4] Vosburgh, THIS JOURNAL, **42**, 1697 (1920).

[5] Tollens, *Ber.*, **17**, 2238 (1884).

[6] Browne, *J. Ind. Eng. Chem.*, **2**, 526 (1910).

Similarly, the formula giving the temperature correction for the specific rotation of invert sugar, valid for 15° to 37°, is found to be

$$[\alpha]^t_D = [\alpha]^{20}_D + (0.283 + 0.0014\,c)\,(t - 20) \qquad (4)$$

Gubbe[7] gives the following formula for the temperature correction between 0° and 30°.

$$[\alpha]^t_D = [\alpha]^{20}_D + 0.30406\,(t - 20) + 0.001654\,(t - 20)^2 \qquad (5)$$

Table I shows a comparison between Vosburgh's observations at 25°, and the corresponding values calculated from Equations 3 and 4, as well as 3 and 5.

TABLE I

VOSBURGH'S OBSERVED AND CALCULATED ROTATIONS OF INVERT SUGAR SOLUTIONS

Invert sugar, g. per 100 cc.	α^{25}_D obs.	α^{25}_D calcd. (3) and (4)	α^{25}_D calcd. (3) and (5)
5.264	−1.93	−1.929	−1.917
10.532	−3.905	−3.920	−3.905
15.800	−5.95	−5.963	−5.952
20.012	−7.625	−7.627	−7.625

The agreement between observed and calculated values is better even than that found by Vosburgh for his equation giving the specific rotation of fructose itself.

Turning now to previous literature, Lippmann[8] quotes the results of six authors who investigated the rotation of invert sugar about 35 to 40 years ago, and he adds that their results show very poor agreement. A critical study of the original papers easily reveals the reason for the discrepancies.

Three of the six authors cited by Lippmann, namely, Burkhard, Bornträger, and Hammerschmidt, used saccharimeters in their investigations. Gubbe and Ost worked with polarimeters, while Landolt put one of Gubbe's formulas into a different form.

Burkhard[9] endeavored to prepare a pure invert sugar solution by heating a sucrose sirup with sulfuric acid (480 g. of sucrose and 100 cc. of sulfuric acid, d. 1.25, per liter) first to 50°, then to 68°, cooling in ice water, precipitating with the necessary quantity of barium hydroxide, and filtering. The concentration naturally had changed during these operations, and in order to determine it anew, he diluted a sample with water until it gave him a saccharimetric reading, at the temperature of 0°, of —27.65° V., corresponding to 44.1° on the French scale. This was the value found by Clerget for invert sugar, but in the presence of hydrochloric acid. Burkhard overlooked this fact, and thought that his reading proved his concentration to be that of pure invert sugar corresponding to the French

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[7] Gubbe, *Ber.*, **18**, 2207 (1885).

[8] Lippmann, "Chemie der Zuckerarten," Friedrich Vieweg und Sohn, Braunschweig, 3d ed., **1904**, Vol. I, p. 920.

[9] Burkhard, *N. Z. Rüben-Zuckerind.*, **14**, 176 (1885).

normal weight of sucrose. Aside from the fact that Burkhard's sirup, judging from his mode of preparation, must have contained reversion products, his observations are rendered valueless by the above assumption. It is, therefore, unnecessary even to consider the equation which he calculated in circular degrees on the basis of his saccharimetric observations, using the factor 0.34578:

$$[\alpha]^{20}_{\mathrm{D}} = -(27.19 + 0.004995\,p - 0.002391\,p^2) \qquad (6)$$

Bornträger,[10] from whom Lippmann quotes a series of values for the specific rotation of invert sugar solutions ranging in concentration from 5 to 60% by weight, prepared his invert sugar sirups by a method similar to that of Burkhard, and determined the concentration by copper reduction. However, the object of his investigation was not to establish the specific rotation of invert sugar, but merely to show that in the determination of invert sugar in sweet Italian wines by saccharimetric methods, an average value of the specific rotation could be used without serious error. He prepared various dilutions of his original sirups and proved with the saccharimeter that, as far as his purpose was concerned, the specific rotation of invert sugar does not change materially with concentration. The series of figures mentioned above, and reprinted in Lippmann's, was calculated from Gubbe's formula II (see below).

The equation that Lippmann quotes as based on Hammerschmidt's[11] work, namely,

$$[\alpha]^{20}_{\mathrm{D}} = -(20.07 + 0.041\,c) \qquad (7)$$

is derived from the latter's saccharimetric measurements on sucrose inverted with hydrochloric acid. Naturally, the values calculated from this formula are very much higher than those for pure invert sugar, and the above equation is, like Burkhard's, useless for our purpose.

Gubbe[7] started from the premise that it is impossible to prepare pure invert sugar from sucrose, there being no way to eliminate the acid used for inversion without in some way altering the properties of the invert sugar formed. He found, however, that while hydrochloric and sulfuric acids increased the levorotation of invert sugar, oxalic acid apparently had no effect on the rotation, as he obtained the same results whether he inverted with 0.13% or with 4.29% of this acid, varying in each case the time of heating so as to get maximum rotation. In his final series of ten tests he used 1% oxalic acid calculated on the basis of the invert sugar, and a temperature of 60–63°. His concentrations ranged from 9.082 to 67.984% of invert sugar by weight, and only the first of them is within the range of Vosburgh's series, while the second is just beyond Vosburgh's highest concentration. A comparison of his results with the figures calculated

[10] Bornträger, *Z. angew. Chem.*, **3**, 481 (1889).

[11] Hammerschmidt, *Z. Ver. deut. Zucker-Ind.*, **41**, 157 (1891).

from Equation 3 is given in Table II, those for $c = 21.5810$ being given in parentheses.

TABLE II

COMPARISON BETWEEN ROTATIONS OBSERVED BY GUBBE AND THOSE CALCULATED FROM VOSBURGH'S RESULTS

Invert, sugar g. per 100 cc.	α_D^{20} obs.	α_D^{20} calcd.	$[\alpha]_D^{20}$ obs.	$[\alpha]_D^{20}$ calcd.
9.3965	− 8.250	− 8.289	−19.983	−20.030
(21.5810)	(−19.364)	(−19.664)	−20.437)	(−20.689)

These values show that Gubbe's results are appreciably lower than Vosburgh's, very probably owing to reversion on account of the extended heating period, which was several hours. Gubbe himself found, by diluting his higher concentrations to 9.3965 g. per 100 cc. and polarizing again, that the diluted products gave lower rotations than the original solution of the concentration 9.3965 g. per 100 cc. These discrepancies increased with the concentration. For this reason he made the necessary corrections on this basis in calculating his Equation I,

$$[\alpha]_D^{20} = -(23.305 - 0.01648\,q - 0.000221\,q^2) \qquad (8)$$

or, as recalculated by Landolt[12] on the basis of p,

$$[\alpha]_D^{20} = -(19.447 + 0.06068\,p - 0.000221\,p^2) \qquad (9)$$

Gubbe assumed that at his lowest concentration no reversion had taken place, but he had no reason for this assumption, and Vosburgh's figures show that it was erroneous.

Remembering that, on account of the oxalic acid present in his solutions, the water concentration in each was lower than if the total solids had been only invert sugar, he made correction for this circumstance in his Equation II,

$$[\alpha]_D^{20} = -(23.305 - 0.01612\,q - 0.00022391\,q^2) \qquad (10)$$

which, on the basis of p becomes:

$$[\alpha]_D^{20} = -(19.454 + 0.06092\,p - 0.00022391\,p^2) \qquad (11)$$

On the further assumption that reversion had not caused a serious error in his results up to a concentration of 35 g. per 100 cc., he established his Equation III for c, on the basis of his original observations, and without applying any corrections. This equation reads,

$$[\alpha]_D^{20} = -(19.657 + 0.03611\,c) \qquad (12)$$

We now know that, besides the errors recognized by Gubbe himself, and for which he made only partial correction, there also is an appreciable effect of oxalic acid on the rotation of invert sugar. Although Ost[13] confirmed Gubbe's experimental results, nevertheless Jungfleisch and Grim-

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[12] Landolt, *Ber.*, **21**, 191 (1888).

[13] Ost, *Ber.*, **24**, 1636 (1891).

bert,[14] as well as Wohl,[15] and also Hammerschmidt[11] disagreed with his conclusions on this point. Later it was demonstrated by Neumann and Wender[16] that oxalic acid increases numerically the rotations of both glucose and fructose, but that there is only partial compensation, as a result of which oxalic acid does increase the levorotation of invert sugar. Since, in spite of this fact, Gubbe's results, even at the lowest concentration used by him, are too low, the reversion which had taken place during the heating was even greater than would appear from his values.

Ost,[13] who shortly after Gubbe's publication investigated the specific rotation of fructose, applied his results also to the question of the specific rotation of invert sugar. He states, very logically, that the best way to prepare pure invert sugar is to mix equal parts of pure glucose and fructose. He proceeded on this basis, and his observations are recorded in Table III, which also gives the values calculated from Equation 3.

TABLE III

COMPARISON BETWEEN ROTATIONS OBSERVED BY OST AND THOSE CALCULATED FROM VOSBURGH'S RESULTS

Invert sugar, g. per 100 cc.	α_D^{20} obs.	α_D^{20} calcd.	$[\alpha]_D^{20}$ observed	$[\alpha]_D^{20}$ calcd.
2.1163	− 1.69	− 1.656	−19.990	−19.562
9.9735	− 8.06	− 8.006	−20.220	−20.066
13.7150	−11.12	−11.120	−20.266	−20.282
15.7050	−12.91	−12.812	−20.548	−20.391

Ost's concentrations are all within the range studied by Vosburgh. It is found that his observed values average higher than those based on Vosburgh's work. This is due to the fact that the fructose used by him gave, within the concentration range indicated above, higher observed values than found by Vosburgh, while his dextrose showed a lower rotation than Tollens had found.

Ost established, on the basis of his results, the equation

$$[\alpha]_D^{20} = -(19.82 + 0.04p) \qquad (13)$$

It is interesting to note that when Ost calculated the rotation of his invert sugar solutions from the rotations of glucose and fructose according to the partial concentration rule, he obtained, like Vosburgh, lower results than those observed by him, but he considered the agreement sufficient to prove the old rule.

Ost also repeated some of Gubbe's experiments on the inversion of sucrose. He found that Gubbe had worked under the best conditions that could be devised for inversion with oxalic acid, and that the specific rotations resulting were only slightly (about 0.2) lower than those found for glucose-fructose mixtures. In one case he even obtained exact agreement; here

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[14] Jungfleisch and Grimbert, *Compt. rend.*, **108**, 144 (1889).

[15] Wohl, *Ber.*, **23**, 2090 (1890).

[16] Neumann and Wender, *Biochem. Z.*, **30**, 357 (1911).

13.024 g. of sucrose per 100 cc. was inverted with 1% oxalic acid by heating for three hours to 50–53°. However, when he used 2.86 g. of oxalic acid at room temperature, his result was appreciably higher, probably due to the effect of the oxalic acid on the rotation of invert sugar, which he denied.

The effect of the various sources of error just discussed on the results of Gubbe's and Ost's figures is best shown in Table IV, in which the values for various concentrations calculated from their equations are compared with one an other and with those resulting from Equation 3.

TABLE IV

COMPARISON BETWEEN SPECIFIC ROTATIONS CALCULATED FROM GUBBE'S AND OST'S EQUATIONS AND THOSE CALCULATED FROM VOSBURGH'S RESULTS

C	Gubbe No. I	Gubbe No. II	Gubbe No. III	Ost	Equation 3
2.5	(19.596)	(19.604)	(19.747)	19.919	19.589
5.0	(19.740)	(19.748)	(19.838)	20.016	19.754
7.5	(19.878)	(19.887)	(19.928)	20.112	19.914
10.0	20.012	20.021	20.018	20.206	20.067
12.5	20.140	20.150	20.108	20.298	20.214
15.0	20.265	20.274	20.199	20.388	20.353
17.5	20.385	20.395	20.289	(20.477)	20.486
20.0	20.500	20.511	20.379	(20.567)	20.612

The values for concentrations outside of the experimental range are again given, as has been done by previous authors, but they are placed in parentheses. It is noted for all the remaining figures, that Gubbe's equations give low results, and Ost's equation high results, for reasons already fully discussed.

The values given under Gubbe No. III, are also to be found in Landolt's book,[17] but he erroneously states that they were calculated from Gubbe's Formula I.

The specific rotation of pure invert sugar has an important bearing on what may be termed the negative component of the "fundamental" Clerget divisor. This negative component may be defined as twice the rotation, in Ventzke degrees, at a temperature of 20.0°, of 13.6842 g. of invert sugar, weighed in air with brass weights, and dissolved to 100 ml. Its value has been determined by Jackson and Gillis,[18] from the results obtained with mixtures of invert sugar and acid by extrapolation to zero acid, to be —32.00 on the Bates and Jackson saccharimeter scale, or —31.97 on the present Schönrock scale. The same authors have pointed out that it can also be calculated by correcting the value found by invertase inversion for the rotation of the invertase itself, and that Browne[19] has reported this to be —32.00 on the Schönrock scale. Sazavsky[20] gives

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[17] Ref. 8, p. 264.

[18] Jackson and Gillis, *Bur. Standards Sci. Paper*, **375** (1920).

[19] Browne, *J. Assoc. Official Agr. Chem.*, **2**, 134 (1916).

[20] Sazavsky, *Z. Zuckerind. cechoslovak. Rep.*, **48**, 259 (1924).

—31.97, supposedly on the same scale. However, recent investigations have raised some doubt as to whether different invertase preparations will always give the same value for the rotation of invert sugar when corrected as indicated. It seemed desirable, therefore, to check the values 32.00 and 31.97 against the specific rotation of pure invert sugar.

From Formula 3, based on Vosburgh's rule, we obtain for the specific rotation at the D line of the weight of invert sugar corresponding to the half-normal weight of sucrose, reduced to a vacuum, in 100 ml., the value —20.281°. The actual rotation at this concentration is therefore —5.554°. If we convert this rotation into Ventzke degrees by the sucrose factor 0.34657 and multiply by 2, we obtain for the negative component of the fundamental Clerget divisor the value 32.05. However, it is well known that the conversion factor is not the same for different sugars, owing to differences in rotation dispersion. Landolt[21] reports for invert sugar the factor 0.3432, and this would give a value for the above, mentioned constant of 32.37. Since Landolt's conversion factor yields such an extreme figure, we have made a series of observations on an invert sugar sirup prepared from sucrose by means of invertase. The very small quantity of impurities introduced by the invertase itself would certainly not exert any noticeable influence on the rotation dispersion of the invert sugar. The measurements were made by filling two jacketed polariscope tubes with the same solution of invert sugar, placing one in the trough of a Bates saccharimeter, and the other in a Schmidt and Haensch polarimeter with sodium light, the two instruments being located side by side in the constant temperature room at 20°. The readings were made simultaneously on both instruments by two observers, then the tubes were exchanged, a new series of readings was taken, and the results were averaged. Four complete such tests, at a concentration corresponding to about —15° V., gave an average factor of 0.34615, decreasing to 0.3460 at —81° V. Using the factor 0.34615, the negative component of the fundamental Clerget divisor becomes 32.09.

It would appear, therefore, that the figure 32.00 is a little low, and this conclusion coincides with that reached at the United States Bureau of Chemistry.[22]

The writer desires to express his thanks to Mr. G. H. Hardin for assistance in the experimental work.

Summary

A critical study of the literature shows that Burkhard's, Bornträger's, and Hammerschmidt's figures cannot be used for establishing an equation for the specific rotation of pure invert sugar. It is also found that Gubbe's

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[21] Ref. 12, p. 194.

[22] Balch, "The Determination of Sucrose and Raffinose in Beet Products by the Enzyme Method," Presented at the Washington Meeting of the American Chemical Society, April, 1924.

values are low, and Ost's high, as compared with the best available information. Landolt's equation is the result of converting Gubbe's formula for q into one for p. From Vosburgh's data for fructose, Tollens' for glucose, and from Vosburgh's rule concerning the rotation of sugar mixtures, the following equation is developed; $[\alpha]^{20}_{D}$ of invert sugar = $-(19.415 + 0.07065c - 0.00054c^2)$.

Vosburgh's experimental figures agree well with this formula. The temperature-correction formula is found to be $[\alpha]^{t}_{D} = [\alpha]^{20}_{D} + (0.283 + 0.0014c)(t-20)$. The first formula gives $-5.554°$ circular for the rotation of the inverted half-normal weight of sucrose in 100 ml. at 20°. By converting this into the negative constituent of the Clerget divisor for pure invert sugar by means of the general factor 0.34657, a value of 32.05 is obtained. Landolt's conversion factor for invert sugar, 0.3432, results in the extremely high value 32.37. In a redetermination of this conversion factor for invert sugar 0.34615 was found, from which 32.09 is obtained. It appears that the accepted value of 32.00 is slightly too low.

[Contribution from the Laboratory of Organic Chemistry of the State University of Iowa]

THE EFFECT OF THE ACIDITY OF ACYL UPON THE MIGRATION FROM NITROGEN TO OXYGEN IN ORTHO-AMINOPHENOLS[1]

By L. Charles Raiford and H. P. Lankelma

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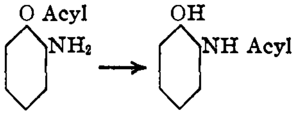
The work of Böttcher,[2] Ransom,[3] Einhorn and Pfyl,[4] and Auwers[5] has shown that, in general, the O-esters of *o*-aminophenols are not capable of existence, and when formed rearrange to the corresponding N-acyl derivatives, in which case the acyl wanders from oxygen to nitrogen. In subsequent papers Auwers and collaborators[6] prepared mixed diacyl derivatives of 2-amino-4-methylphenol, and assumed that the radical last introduced



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[1] Condensed from a thesis presented by H. P. Lankelma to the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Böttcher, *Ber.*, **16**, 629 (1883).

[3] Ransom [*Ber.*. **31**, 1055 (1898); **33**, 199 (1900); *Am. Chem. J.*, **23**, 1 (1900)] found that under special conditions he could isolate the O-ester of carbonic acid.

[4] Einhorn and Pfyl, *Ann.*, **311**, 34 (1900).

[5] Auwers, *Ber.*, **33**, 1923 (1900).

[6] See Auwers and Eisenlohr, *Ann.*, **369**, 209 (1909).