[CONTRIBUTION FROM THE GOVERNMENT CHEMICAL INDUSTRIAL RESEARCH INSTITUTE, TOKYO]

The Specific Rotation of Fructose

BY Y. TSUZUKI, J. YAMAZAKI[1] AND K. KAGAMI

The specific rotation of fructose has been measured by a number of investigators.[2–6] However, the range of these measurements is relatively short, namely, the highest temperature is 44.6°. Our investigation on this subject has two aims. One of them is to give data for higher temperatures above 40°, since it was necessary, in our studies (not yet published) on the sweetness and chemical constitution of fructose, to get information as to how the equilibrium between the various forms of fructose shifts with temperature. The second aim is to extend measurements with very pure materials to wider ranges of temperature and concentration, and thus to present a whole series of precise data so as to make the determination of the quantity or of the purity of fructose possible by polarimetric methods, for there lack in chemical literature systematic measurements of the specific rotation of fructose in spite of its exceptional sensitivity to temperature and concentration.

Experimental

Purification of Fructose.—We have used crystalline (D-β-)fructose "for medical use" produced by the Japan Fructose Company as the starting material. It is prepared from Jerusalem artichoke and is free from glucose, having a purity over 99.7%.

For purification this sugar was recrystallized from water as follows: 500 g. of fructose was dissolved in an equal weight of water, treated with 5 g. of carbon (previously washed with water in order to remove any soluble inorganic matter), filtered and evaporated under reduced pressure at 45 to 50° until a thick sirup of 90% ($n^{20}\mathrm{D}$ 1.51) was obtained. After cooling to 40° the sirup was seeded and kept at this temperature for twenty to thirty hours with occasional stirring until it grew into a massecuite (or viscous crystalline suspension). The crystals were separated by a centrifuge, washed with a small quantity of water and dried *in vacuo* over concentrated sulfuric acid to a constant weight. Thus a highly pure sample of anhydrous fructose (200 g.) was obtained as dry and sandy crystals consisting of tilted cubes of a nearly uniform size about 0.5 mm.

Besides this we have tried the purification in several ways, namely, by recrystallizing from dilute alcohol, from acetic acid, from water and then from alcohol, etc. Estimating the purity by polarimetric measurements, we have come to the conclusion that a single crystallization is sufficient to obtain a pure sample of fructose, although a negligible quantity of mineral matters is still included. This cannot be eliminated merely by recrystallizing from water, but is entirely removed by the use of dilute alcohol. By recrystallizing from water and then from 50% alcohol we were able to obtain easily a sample of highest purity. It is seen, however, in Table I that there is no significant difference in the different preparations with respect to specific rotation.

TABLE I

PURIFICATION OF FRUCTOSE

Fructose prepn.	Recrystallized from	Melting point, °C.	Ash, %	$[\alpha]^{20}\mathrm{D}(p = 20)$
Commercial		103	0.028	−94.07
1	Water	104	.007	−94.38
2	Water, 2 times	104	.004	−94.31
3	Water, 3 times	104	.003	−94.37
7	Acetic acid	...	.002	−94.47
11	Water and then from alcohol	104	.000	−94.40

Eleven different samples of fructose thus carefully purified were taken for our measurements.

Method of Measurement.—We have observed the angles of rotation by a triple-field polarimeter with an accuracy of 0.01 to 0.02° using an enclosed sodium lamp as the light source and two types of polarimeter tube for temperature control. One of them is a glass tube enclosed in a metal jacket through which water at a constant temperature may be circulated from a thermostat, and the other a brass tube enclosed in a small metal thermostat which can be heated from outside. The latter was always used for the measurements at 0° and at higher temperatures above 60°. The temperature was in every case maintained constant within ±0.05°. The length of the tubes is 1 dm.[7] and corrected at each temperature to ±0.02 mm.

Measurements on the rotation as well as on the density were made after the solution had been allowed to stand at the temperature of measurement long enough for mutarotation to have been completed. This took at least two hours at 0°, forty minutes at 10°, and fifteen minutes at 20°.

It was confirmed that fructose suffers no appreciable decomposition during the measurements at higher temperatures, for we observed practically the same values of rotation at respective temperatures on warming the solution gradually from zero to 90°, and reversely cooling down to lower temperatures.

Results of Measurements.—We have measured the specific rotation of fructose systematically at different temperatures from zero up to 90°, and at various concentrations from 5 to 40%. The results of measurements were collected in Table III, where p gives percentage by weight (g. of fructose in 100 g. of solution). Each of the values is the mean of several observations of different preparations. Some examples are presented in Table II to show the precision of the measurements. The values of observed rotation, α_{D}, are given per 1.000 dm. of the length of the column of solution. Densities were measured by means of an Ostwald pyknometer with a capacity of about 5 cc. All weights were reduced to vacuum.

In order to get a view on the general trend how the values of the specific rotation of fructose vary with temperature and concentration, the values in Table III are shown in Fig. 1, where some

---

(1) Principal research chemist of the Japan Fructose Company, Kawasaki.

(2) Jungfleisch and Grimbert, *Compt. rend.*, **107**, 392 (1888).

(3) Ost, *Ber.*, **24**, 1618 (1891).

(4) Hönig and Jesser, *Monatsh.*, **9**, 568 (1889).

(5) Nelson and Beegle, THIS JOURNAL, **41**, 564 (1919).

(6) Vosburgh, *ibid.*, **42**, 1696 (1920).

(7) Sometimes a polarimeter tube of 2 dm. length was also used, especially at lower concentrations below 10%.

Table II

Some Examples of Data of Measurements

Fructose, prepn.	p	d_4	α_D	$[\alpha]_D$
		(1) Temperature, 20.0°		
1	20.014	1.0816	−20.43	−94.38
2	19.994	1.0819	−20.40	−94.31
3	19.993	1.0818	−20.41	−94.37
11	19.995	1.0817	−20.42	−94.40
		(2) Temperature, 50.0°		
1	9.9960	1.0270	− 7.73	−75.30
4	9.9958	1.0270	− 7.74	−75.39
10	9.9959	1.0263	−15.45 (2 dm.)	−75.30
		(3) Temperature, 80.0°		
9	40.003	1.1389	−27.82	−61.05
10	39.992	1.1383	−27.745	−60.95

Table III

Specific Rotation of Fructose

t, °C. / p(%) →	5	10	15	20	30	40
0	−103.25	−104.09	−104.87	−105.27	−106.63	−108.19
10	−98.49	−98.57	−99.52	−100.22	−101.36	−102.85
15	−95.49	−95.99	−96.95	−97.34	−98.51	−100.08
20	−92.49	−93.17	−93.72	−94.37	−95.66	−97.11
25	−89.53	−90.02	−90.76	−91.42	−92.78	−94.09
30	−86.69	−87.24	−87.70	−88.43	−89.62	−91.08
40	−80.62	−81.20	−81.73	−82.41	−83.65	−84.95
50	−74.57	−75.33	−75.88	−76.33	−77.54	−78.73
60	−68.63	−69.27	−69.86	−70.58	−71.53	−72.82
70		−63.50	−64.00	−64.44	−65.67	−66.92
80		−57.62	−58.26	−58.81	−59.82	−61.00
90		−51.75		−52.74		−55.41

omissions (of 5 and 15%) are made for the sake of clarity.

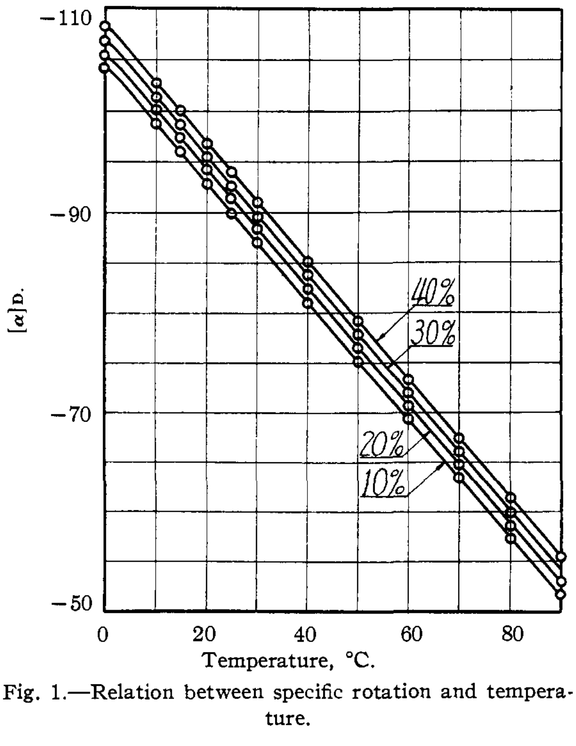

Fig. 1.—Relation between specific rotation and temperature.

It may be seen in Fig. 1 that the relation between the specific rotation and temperature is invariably linear in the temperature range above 10°. It is also worthy of note that the specific rotation increases with concentration and that these straight lines run nearly parallel with an approximately constant distance.

The values for densities of aqueous solutions of fructose are summarized in Table IV. No data covering such a wide range as these are known in the literature except the very detailed measurements by Jackson and Mathews,[8] which are, however, limited to 20° and 25°.

Table IV

Densities of Aqueous Solutions of Fructose

t / p →	5	10	15	20	30	40
0	1.0202	1.0409	1.0633	1.0860	1.1348	1.1868
10	1.0201	1.0410	1.0618	1.0842	1.1322	1.1825
15	1.0191	1.0398	1.0607	1.0826	1.1301	1.1802
20	1.0180	1.0386	1.0593	1.0817	1.1276	1.1778
25	1.0167	1.0371	1.0576	1.0793	1.1253	1.1748
30	1.0149	1.0352	1.0560	1.0774	1.1229	1.1720
40	1.0112	1.0315	1.0519	1.0733	1.1183	1.1663
50	1.0070	1.0268	1.0465	1.0677	1.1125	1.1603
60	1.0014	1.0214	1.0400	1.0626	1.1065	1.1525
70		1.0151	1.0343	1.0551	1.0991	1.1460
80		1.0090	1.0281	1.0486	1.0922	1.1386
90		1.0016		1.0414		1.1314

By using the data given in Tables III and IV we are able to express the specific rotations in term of volume percentage, c, and since their variations due to temperature and concentration are quite regular, it is possible, by interpolation, to calculate the values of the specific rotation for any concentration and temperature in the above limits with an error usually less than 0.05°. Thus we can compare our results of measurements with those of the previous observers, which were often given in term of percentage by volume. In Table V are shown some examples of our calculations, and the results compared with the data of Vosburgh,[6] which are the highest values found in the literature. It is seen from this Table that our values are somewhat higher than those of Vosburgh.

Table V

Temp., °C.	The present authors			Vosburgh	
	c	$[\alpha]_D$	$[\alpha]_D$ calcd.	c	$[\alpha]_D$
		For c = 10.00			
20	10.386	−93.17	−93.14	10.028	−92.94
25	10.371	−90.02	−89.99	10.006	−89.90
30	10.352	−87.24	−87.21	10.006	−86.90

Empirical Formula.—The specific rotation of fructose can be expressed by means of the equation

$$[\alpha]^t_D = -(103.6 + 0.134p) + (0.59 + 0.0003p)t \quad (1)$$

where p is concentration by weight percentage.

---

[8] Jackson and Mathews, *Bur. Standards J. Research*, **8**, 403 (1932).

This equation is based on our experimental results for $p = 5$ to 40% and $t = 10$ to 90°.

It is a remarkable and rather singular fact that any t^2-term is unnecessary to express with fair accuracy the wide variations due to temperature of the specific rotation of fructose from 10 to 90°.

The difference between the calculated and the found in the values of $[\alpha]_D$ lies in most cases under 0.1°. This empirical formula covers a wider range as compared with those previously proposed.[9] Moreover, it gives always higher values. That will be evident, if one compares, for instance, the following formulas (2) and (3) derived as special cases from our original equation (1) respectively with that of Ost–Vosburgh[9] and Vosburgh's second equation[9] (both giving highest values among the previously presented).

$$[\alpha]^{20}D = -(91.80 + 0.140p) \qquad (2)$$

$$[\alpha]^{25}D = -(88.85 + 0.1415p) \qquad (3)$$

As seen from the above statement these equations as well as the data obtained for the specific rotation of fructose may be available for estimating the purity of any sample of fructose with the accuracy of 0.1% by measuring polarimetrically at any temperature and concentration.

Summary

The specific rotation of fructose has been measured accurately and systematically at temperatures from 0 to 90°, and for concentrations from 5 to 40%. The values are without exception higher than those of previous investigators.

The specific rotation can be expressed by an equation

$$[\alpha]^tD = -(103.6 + 0.134p) + (0.59 + 0.0003p)t$$

for $p = 5$ to 40% and for $t = 10$ to 90°.

TOKYO-HATAGAYA, JAPAN RECEIVED JULY 27, 1949

[9] Mention will be made of some important ones: the equation of Jungfleisch and Grimbert is valid for $t = 0$ to 40° and for c below 40%, that of Hönig and Jesser (*J. deut. Zuckerind.*, **38**, 1028 (1888)) for $p = 4$ to 40% and for $t = 12$ to 45°, that of Ost-Vosburgh: $[\alpha]^{20}D = -(91.50 + 0.133\,p)$ for $p = 3$ to 30%, that of Vosburgh: $[\alpha]^tD = [\alpha]^{25}D + (0.566 + 0.0028\,c)(t - 25)$ for $c = 5$ to 10% and for $t = 15$ to 37°, and Vosburgh's second equation: $[\alpha]^{25}D = -(88.50 + 0.145p)$ for $p = 2.6$ to 18.6%.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Preparation of Unsaturated Sulfones by Condensation Reactions[1]

BY SAUL CHODROFF[2] AND WILLETT F. WHITMORE

Tröger has found that aromatic aldehydes condense with phenylsulfonylacetic acids under conditions of the Perkin reaction,[3] and with sulfonylacetonitriles in the presence of alkali,[4] or pyridine[5] in alcoholic solution. It was felt that *p*-tolylsulfonylacetic acid could be substituted for malonic acid in the Doebner modification of the Knoevenagel reaction, to yield unsaturated sulfones of the type $p\text{-}CH_3C_6H_4SO_2CH{=}CHR$. The reaction was carried out by heating the acid with the carbonyl component in pyridine in the presence of piperidine for six hours, or until carbon dioxide evolution ceased. It was found that few carbonyl compounds reacted unequivocally to yield the unsaturated sulfone, the complicating feature of the reaction being the competitive decarboxylation of the acid to yield *p*-tolylmethyl sulfone.[6] Of the compounds studied, only cinnamaldehyde and benzaldehyde yielded isolable unsaturated sulfones. Aliphatic aldehydes, aliphatic and aromatic ketones yielded only the methyl sulfone and the unreacted carbonyl component under these conditions. The procedure of Schwenk and Papa,[7] employing triethylamine in acetic anhydride as a condensation medium, has not been found applicable for the preparation of unsaturated sulfones.

Using the procedure of Cope,[8] ethyl *n*-butylsulfonylacetate was condensed with both aliphatic and aromatic aldehydes, the theoretical amount of water being evolved in thirty minutes to two hours. Only in the case of chloral, which required the use of ammonium acetate instead of piperidine acetate, was the reaction time prolonged to twenty-three hours. Aliphatic and aromatic ketones failed to react with this ester under a variety of conditions, which included the use of such catalysts as piperidine acetate, ammonium acetate, triethylamine acetate and morpholine acetate. Other conditions used without success were prolonged refluxing with potassium acetate and acetic anhydride, and reaction in the presence of zinc chloride and acetic anhydride. In all cases, the original ester was recovered unchanged. The α-

[1] The material for this paper was abstracted in part from the thesis of S. Chodroff submitted to the Faculty of the Graduate School of the Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1948.

[2] Present address: Rare-Galen Division, Nopco Chemical Company, Harrison, New Jersey.

[3] Tröger and Hille, *J. prakt. Chem.*, [2] **71**, 201 (1905).

[4] Tröger and Prochnow, *ibid.*, [2] **78**, 123 (1908).

[5] Tröger and Brenner, *Arch. Pharm.*, **247**, 613 (1910).

[6] Usually more vigorous conditions are required for the decarboxylation of the α-alkylsulfonylcarboxylic acids; for example, Otto and Otto (*Ber.*, **21**, 992 (1888)) found that α-ethylsulfonylpropionic acid yielded diethyl sulfone at 200°, and Tröger and Uhde (*J. prakt. Chem.*, [2] **59**, 334 (1899)) prepared phenylisopropyl sulfone by heating α-phenylsulfonylisobutyric acid with potassium hydroxide at 170°. It is only when these acids have one or more halogens attached to the α-carbon atoms, that the loss of carbon dioxide takes place at a lower temperature. Fouque and LaCroix, *Bull. soc. chim.*, **33**, 180 (1923), and Otto, *J. prakt. Chem.*, [2] **40**, 527 (1889).

[7] Schwenk and Papa, THIS JOURNAL, **67**, 1432 (1945).

[8] Cope and Hofman, *ibid.*, **63**, 3456 (1941); Cope, Hofman, Wycoff and Hardenbergh, *ibid.*, **63**, 3452 (1941).