When the run was worked up in the usual manner no valeroin was found. On the other hand, 50% of the valeric acid was recovered from the alkaline water layer.

Summary

Detailed directions are given for the preparation of aliphatic acyloins. Approximately 50% yields of the following acyloins were obtained: propionoin, *n*-butyroin, isobutyroin, *n*-valeroin, isovaleroin, *n*-capronoin, isocapronoin, 3,8-dimethyldecanol-5-one-6 and 3,3,6,6-tetramethyl-octanol-4-one-5. The last three substances are new.

Aliphatic acyloins easily undergo photochemical decomposition.

MIDDLEBURY, VERMONT

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXX. THE COMPARATIVE HYDROLYSIS OF SOME DISACCHARIDES AND POLYSACCHARIDES

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Introduction

The problem of the relative ease of hydrolysis of disaccharides and of polysaccharides such as starch and cellulose is an important one, not only from the scientific, but also from the industrial standpoint. Thus its solution is of great importance for a thorough understanding not only of the role played by starch as a "reserve material" in the vegetable kingdom but also of the close inter-relationship existing between starch and cellulose in plant metabolism. Also since it may be assumed that the structure of cellulose as a long chain of cellobiose units is now established on a reasonably firm basis, and that starch is presumably derived in a similar manner from maltose, the inter-relation of the reactions involving both analysis and synthesis of these products is of considerable interest.

It would also seem that a more intimate knowledge of the relative ease of hydrolysis of these products into glucose might throw some light on their relative stability and the bearing of the latter on the mode of linkage in the long-chain polysaccharides. Many of these hydrolytic changes, as shown in other researches to be published later, can be readily brought about under the influence of bacterial action as well as by the enzyme isolated from such organisms. There thus exists the possibility of co-relating two widely different types of hydrolytic agents.

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Part I. Hydrolysis of Derivatives of Glucopyranose

The hydrolysis of starch by dilute acids has been investigated by Nanji and Beazeley,[2] Defren,[3] Meyer, Hopff and Mark[4] and others. Similarly Sherrard and Gauger,[5] Ost and Wilkening[6] and Simonsen[7] have studied the hydrolysis of cellulose by dilute acid. Since heat has to be applied, however, there is extensive decomposition of the glucose formed and the results are of no interest for comparing the two polysaccharides, the more so as cellulose is not dispersed in dilute acid.

Willstätter and Zechmeister[8] dissolved cotton cellulose in 41% hydrochloric acid and followed the course of the hydrolysis by observing the change in the specific rotation of the solution, and its reducing power. A discontinuity in the curve after about three hours was taken to indicate the presence of cellobiose. Sherrard and Froehlke[9] and Cunningham[10] employed a similar method, and König and Hühn[11] used a solution of zinc chloride in hydrochloric acid to disperse and hydrolyze cellulose.

Daish[12] investigated the hydrolysis of starch and maltose using fuming and concentrated hydrochloric acid, and he compared his results with those of Willstätter and Zechmeister.[8] Although his values indicate that starch hydrolyzes much more rapidly than cellulose, the fact that the experiments were not conducted under comparable conditions detracts from their value for purposes of comparison. Daish[12] indeed showed that maltose was hydrolyzed at about the same speed as starch itself, but as to how far the hydrolysis of cellulose is concerned with the breakdown of cellobiose was still left undecided. Freudenberg, Wolf, Knopf and Zaheer,[13] carrying out hydrolyses with *N* sulfuric acid at 70°, showed that cellobiose is much more difficult to break down than maltose. Willstätter and Zechmeister[8] had also called attention to the resistance towards hydrolysis of this disaccharide.

Selection of Reaction Medium

Instead of the inconvenient, fuming hydrochloric acid, it was decided to use zinc chloride, dissolved in hydrochloric acid, for the experiments on glucopyranose derivatives.

[2] Nanji and Beazeley, *J. Soc. Chem. Ind.*, 215T (1926).

[3] "Eighth International Congress of Applied Chem.," 13, 113 (1912).

[4] Meyer, Hopff and Mark, *Ber.*, 62, 1103 (1929).

[5] Sherrard and Gauger, *J. Ind. Eng. Chem.*, 15, 1164 (1923).

[6] Ost and Wilkening, *Chem.-Ztg.*, **34**, 461 (1916).

[7] Simonsen, *Z. angew. Chem.*, 11, 219 (1898).

[8] Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913).

[9] Sherrard and Froehlke, This Journal, **40**, 173 (1918).

[10] Cunningham, *J. Chem. Soc.*, 113, 173 (1918).

[11] König and Hühn, "Bestimmung der Zellulose in Holzarten," **1912**, p. 55.

[12] Daish, *J. Chem. Soc.*, **105**, 2053 (1914).

[13] Freudenberg, Wolf, Knopf and Zaheer, *Ber.*, **61**, 1743 (1928).

In the case of certain anhydrofructose compounds which were to be investigated, it was found advisable, owing to the rapidity of the hydrolysis and the decomposition of the fructose, to employ 0.1 *N* oxalic acid at 65°.

Preparation of Materials

Cellulose.—The material used was a pure absorbent cotton, having an α-cellulose value of 99.1%; ash, 0.05%, after drying at 60° (15 mm.).

β-Cellobiose.—This disaccharide was prepared from cellobiose octa-acetate (m. p. 227°), by the method of Maquenne and Goodwin,[14] as modified by Haworth and Hirst.[15] The product after purification had $[\alpha]_D^{20}$ 35°; m. p. 215°.

Cellodextrin (Cellobiosan) was prepared by Mr. J. G. Morazain, of this Laboratory, according to the method of Hess and Friese[16] (see also Meyer and Hopff);[17] $[\alpha]_D^{20}$ in 2 *N* NaOH, −4.1°.

Starch.—This was Kahlbaum's pure soluble starch for analysis, dried at 60° (15 mm.).

Inulin.—"Kiliani inulin" was "recrystallized" according to the method of Drew and Haworth[18] and dried at 60° (15 mm.).

Levan.—This was supplied by Mr. R. S. Tipson[19] of this Laboratory, and obtained by the action of *Bacillus mesentericus* on sucrose; after electrodialysis it was precipitated twice with alcohol; $[\alpha]_D^{20}$ −40°, dried at 60° (15 mm.).

The maltose, lactose, glucose, fructose, sucrose and galactose used in these experiments were authentic samples as shown by their physical constants, and were dried over phosphoric oxide in a vacuum.

The solvent, hereafter called (A), used in the experiments on the glucopyranose derivatives was a solution of anhydrous zinc chloride (1 part) in concentrated hydrochloric acid (*d*, 1.180) (2 parts) and was of d_4^{23} 1.464.

For the anhydrofructose derivatives 0.105 *N* oxalic acid (solution B) was used as the hydrolyzing agent.

The optical measurements were made with the Frič polarimeter recommended by the U. S. Bureau of Standards.[20] All solutions were kept at 23 ± 0.1° by the use of a jacketed tube, except when oxalic acid was employed as hydrolyzing agent, in which case the temperature was 65 ± 0.2°.

Throughout these experiments *K* is calculated from the formula

$$K = \frac{1}{0.4343t} \log_{10} \cdot \frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_t}$$

derived from the equation for a monomolecular reaction, in which t is time in seconds, α_0 is initial value of specific rotation (extrapolated), α_∞ is final value of specific rotation and α_t is rotation at time t.

Experimental

For purposes of comparison it is necessary to have the cellulose completely dispersed prior to the hydrolysis and to carry out the experiments

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[14] Maquenne and Goodwin, *Bull. soc. chim.*, **31**, 954 (1904).

[15] Haworth and Hirst, *J. Chem. Soc.*, 119, 193 (1921).

[16] Hess and Friese, *Ann.*, **450**, 40 (1926).

[17] Meyer and Hopff, *Ber.*, **63**, 790 (1930).

[18] Drew and Haworth, *J. Chem. Soc.*, **133**, 2690 (1928).

[19] Hibbert and Tipson, unpublished research. See preliminary note. THIS JOURNAL, **52**, 2582 (1930).

[20] U. S. Bureau of Standards, Bulletin No. 44.

under identical conditions of temperature, because the velocity of a reaction is so markedly influenced by that factor.

The Hydrolysis of Cotton Cellulose at 23°.—About 0.25 g. of the dry material was weighed out accurately into a dry stoppered bottle, and 50 cc. of the solvent (A), at 23°, was added by means of a pipet. The mixture was shaken vigorously for five minutes and then carefully filtered through a weighed asbestos Gooch crucible, taking care to avoid loss of hydrogen chloride by employing the minimum amount of suction. The clear solution was transferred to the polarimeter tube and readings were taken at convenient times until the rotation became constant.

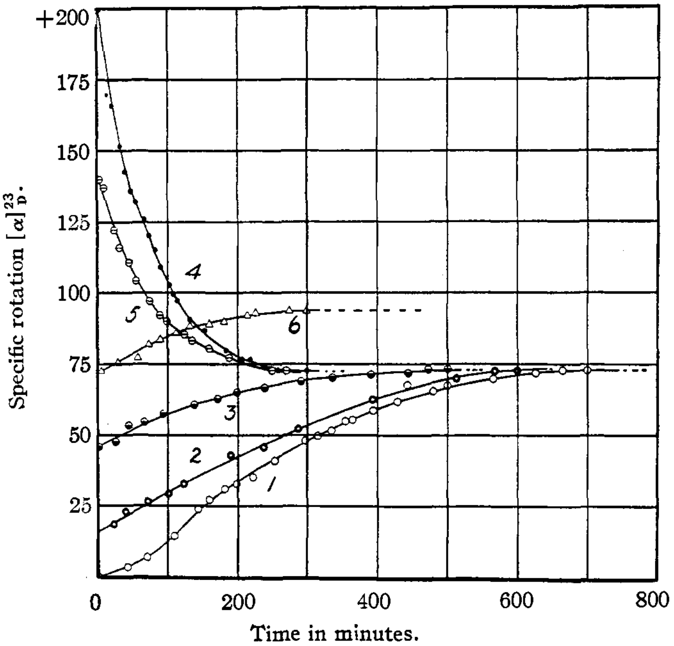

Fig. 1.—Rate of hydrolysis in zinc chloride–hydrochloric acid solution at 23°: 1, cellulose, ○; 2, cellodextrin **O**; 3, cellobiose, ◒; 4, starch, ●; 5, maltose, ⊖; 6, lactose, △.

The Gooch crucible was washed with distilled water and alcohol, dried at 105°, weighed and the increase in weight subtracted from the original weight of cellulose. This method was adopted because otherwise a slight cloudiness obscured the rotation. The amount of insoluble material after five minutes was usually about 7%. $[\alpha]^{23}_D$ was calculated on the basis of glucose, *i. e.*, $[\alpha]^{23}_D$ observed × (162/180).

The rotation of anhydrous glucose in the same solvent (A) gave $[\alpha]^{23}_D$ +73.1 for $C = 1$.

The results are to be found in Table I and are plotted as Curve 1, Fig. 1.

The Hydrolysis of β-Cellobiose at 23°.—This disaccharide is completely soluble in solvent (A) to give a clear solution. The results are to be found in Table II and are plotted in Curve 3, Fig. 1.

TABLE I

THE HYDROLYSIS OF CELLULOSE AT 23°

Concentration, 0.454 g. of cellulose in 100 cc. of solvent (A)

Time, min.	$[\alpha]^{23}_{D}$	$K \times 10^4$	Time, min.	$[\alpha]^{23}_{D}$	$K \times 10^4$
0	0	...	335	51.5	0.61
42	+ 3.4	0.18	355	54.9	.66
75	6.9	.22	365	55.6	.66
105	14.4	.35	392	58.3	.69
156	24.0	.47	429	61.7	.73
160	27.4	.49	479	65.2	.79
182	30.9	.51	502	67.2	.83
199	32.9	.50	565	69.9	.96
223	35.0	.49	625	72.0	1.24
255	41.0	.54	665	72.7	...
298	48.0	.60	700	+72.7	...
315	49.4	.60			

The reaction is thus shown not to be of the monomolecular type. Mean value of $K = 0.61 \times 10^{-4}$.

TABLE II

EXPERIMENTAL RESULTS

Concentration, 0.574 g. of cellobiose in 100 cc. of solvent (A)

Time, min.	$[\alpha]^{23}_{D}$	$K \times 10^4$	Time, min.	$[\alpha]^{23}_{D}$	$K \times 10^4$
0	+46.1	..	136	60.2	0.91
2	46.4	0.90	180	63.0	.93
10	46.5	.89	250	66.5	.95
16	48.7	1.05	296	68.7	1.02
21	49.9	1.20	339	69.3	0.96
37	52.1	1.13	388	70.5	1.00
61	54.4	1.10	449	71.6	1.07
94	56.3	0.95	508	73.1	..
113	59.0	.96	560	+73.1	..

Mean value of $K = 1.0 \times 10^{-4}$. The reaction is of the monomolecular type.

The Hydrolysis of Cellodextrin at 23°.—The results (Table III) indicate that the hydrolysis is not monomolecular, and that the polysaccharide occupies an intermediate position between cellulose on the one hand and cellobiose on the other. The values are plotted in Curve 2, Fig. 1.

TABLE III

EXPERIMENTAL RESULTS

Concentration, 0.550 g. of cellodextrin in 100 cc. of solvent (A)

Time, min.	$[\alpha]^{23}_{D}$	$K \times 10^4$	Time, min.	$[\alpha]^{23}_{D}$	$K \times 10^4$
0	+16.5	..	238	46.0	0.52
12	18.4	0.48	287	52.2	.57
39	22.7	.50	394	62.6	.73
71	26.4	.46	443	67.5	.91
101	29.5	.44	513	69.9	.99
123	32.8	.46	573	72.5	..
190	43.0	.56	600	+72.5	..

The Hydrolysis of Starch at 23°.—Using the same technique, the hydrolysis of starch was investigated. The results are to be found in Table IV and are plotted on Curve 4, Fig. 1.

TABLE IV

EXPERIMENTAL RESULTS

Concentration, 0.448 g. of starch per 100 cc. of solution

Time, min.	$[\alpha]_D^{23}$	$K \times 10^4$	Time, min.	$[\alpha]_D^{23}$	$K \times 10^4$
0	+200.0	..	102	103.0	2.36
12	169.7	3.79	109	98.6	2.05
19	165.6	2.77	114	97.4	2.41
32	151.7	2.49	133	90.4	2.46
39	142.6	2.58	155	87.0	2.58
47	136.0	2.49	185	80.0	2.40
55	132.1	2.32	205	77.0	2.49
66	126.0	2.27	219	76.5	2.73
73	120.0	2.29	258	73.0	..
82	115.6	2.25	300	+73.0	..
90	109.2	2.33			

Mean value of $K = 2.45 \times 10^{-4}$. The reaction is apparently monomolecular after the first half hour.

The Hydrolysis of Maltose at 23°.—The results depicted in Table V and plotted in Curve 5, Fig. 1, indicate that the reaction is monomolecular.

TABLE V

EXPERIMENTAL RESULTS

Concentration, 0.552 g. of maltose in 100 cc. of (A)

Time, min.	$[\alpha]_D^{23}$	$K \times 10^4$	Time, min.	$[\alpha]_D^{23}$	$K \times 10^4$
0	+142.8	..	100	90.0	2.36
2	140.1	..	125	85.3	2.33
9	137.1	1.84	136	83.1	2.37
23	122.2	2.46	160	80.2	2.36
31	116.1	2.68	188	77.4	2.43
45	110.3	2.36	239	74.5	2.60
55	104.2	2.47	250	72.8	..
75	97.2	2.37	270	+72.8	..
90	92.3	2.44			

Mean $K = 2.40 \times 10^{-4}$.

TABLE VI

THE HYDROLYSIS OF LACTOSE AT 23°

Concentration, 1.560 g. of lactose in 100 cc. of solvent (A)

Time, min.	$[\alpha]_D^{23}$	$K \times 10^4$	Time, min.	$[\alpha]_D^{23}$	$K \times 10^4$
0	+72.4	..	133	87.7	2.49
4	72.8	..	161	88.8	2.78
28	73.0	..	182	89.9	2.67
56	76.9	2.80	216	92.0	2.57
73	81.7	2.90	247	92.8	2.83
90	83.4	2.63	275	93.5	..
113	85.4	2.43	300	+93.5	..

Mean value of $K = 2.84 \times 10^{-4}$. The reaction again is of the monomolecular type.

Since the results seemed to indicate that a β-biose is hydrolyzed much more slowly than an α-biose, it appeared of interest to determine whether lactose (which is a β-galactoside) hydrolyzes as slowly as cellobiose. The results are to be found in Table VI and are plotted in Curve 6, Fig. 1.

Discussion of Results

Table VII shows the mean values of the hydrolysis constant K for the substances indicated.

TABLE VII

VALUES OF THE HYDROLYSIS CONSTANT

Substance	Cellobiose	Starch	Maltose	Lactose
$K \times 10^4$	1.00	2.45	2.40	2.84

These experiments establish the fact that no generalization can be made as to the rate of hydrolysis of a disaccharide, and the mode of union of the building units with one another. This was also emphasized by Freudenberg, Wolf, Knopf and Zaheer,[13] who carried out the hydrolyses at 70° in N sulfuric acid solution for a large number of glucosides and disaccharides. These workers showed that under their experimental conditions, maltose (α-linkage) is hydrolyzed more than twice as rapidly as cellobiose (β-linkage) and that lactose (β-linkage) is hydrolyzed a little faster than maltose; this is confirmed by the present results.

The conclusions of Willstätter and Zechmeister[8] with regard to the discontinuity in their curve for the hydrolysis of cellulose are not confirmed in the present instance and it is suggested their results are possibly due to temperature variations. There would appear to be no theoretical significance whatever to the discontinuity as found by these authors. It would mean either that the hydrolysis had stopped, or that a substance of zero or negative rotation was being formed, whereas cellobiose was shown to have a positive equilibrium rotation value in their solvent. It is noteworthy that these authors in their determination of the reducing power found no such steps in the curve, and the same may be said of the results of Sherrard and Froehlke.[9]

The slow hydrolysis of cellulose is due to a great extent to the slow hydrolysis of cellobiose. The reaction is not monomolecular and the hydrolysis constants tend toward the value experimentally found for cellobiose under the same conditions.

If cellobiose is a reversion product as Hess[21] suggests, the time for the hydrolysis would be abnormally long because the following chain of reactions must, in this case, take place

$$\text{Cellulose} \longrightarrow \text{Glucose} \longrightarrow \text{Cellobiose} \longrightarrow \text{Glucose}$$

The fact that the cellobiosan of Hess and Friese[16] (which is regarded as a cellulosedextrin in the recent paper by Meyer and Hopff)[17] occupies an

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[21] Hess, "Die Chemie der Zellulose," Leipzig, Germany, 1928, p. 494.

intermediate position between cellulose and cellobiose is further evidence against Hess' viewpoint.

The observations of König and Hühn, who found maxima in the case of the hydrolysis of different celluloses using solvent (A), are not confirmed except that it is apparent that the maxima they refer to are due to the destruction of glucose on standing, the solution becoming yellow and diminishing in $[\alpha]^t_D$ after thirty hours.

Willstätter and Zechmeister[8] considered that the amount of isomaltose formed in a 1% solution of glucose in fuming hydrochloric acid was negligible. This has been contested by Irvine and Soutar[22] but there seems to be little doubt that in the dilute solution used for these experiments (0.5%) the amount of isomaltose present at equilibrium would not affect the conclusions.

The difference in the rate of hydrolysis of starch and cellulose under identical conditions is shown to be due mainly to the difference in the rates of hydrolysis of the corresponding disaccharides, maltose and cellobiose, respectively. There would seem to be, therefore, no foundation for the belief that the glucose units in these polysaccharides possess a different ring system; the only difference between starch and cellulose, as far as hydrolysis is concerned, would seem to be due to the mode of linking of the glucose residues and the physical nature of the substances (see also Haworth[23] and Meyer, Hopff and Mark[4]).

It has been shown (Table III) that after the first half hour the hydrolysis of starch is practically monomolecular. Daish, using both concentrated and fuming hydrochloric acid, concluded that the hydrolysis of starch was not monomolecular but varied about 20% from that condition. He showed, however, that maltose did follow a monomolecular course and indicated that the two substances were hydrolyzed at almost the same rate. This is confirmed by the present series of observations.

The great influence of concentrated hydrochloric acid on the equilibrium rotation value was pointed out by Daish and has been observed repeatedly by other workers.

In the particular case of the zinc chloride–hydrochloric acid solvent (A) used, the equilibrium rotation between α- and β-glucose is shifted from +52.5 to +73.1°.

Part II

The Hydrolysis of Derivatives of Anhydrofructose.—It was of particular interest to determine the relation of levan to inulin. The former, as shown by Hibbert and Tipson,[19] consists of γ-fructose units linked together in the 2,6-positions. On the other hand, Haworth and Learner[24] provide con-

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[22] Irvine and Soutar, *J. Chem. Soc.*, 117, 1489 (1920).

[23] Haworth, "The Constitution of Sugars," London, 1929, pp. 83, *et seq.*

[24] Haworth and Learner, *J. Chem. Soc.*, 133, 619 (1928).

clusive evidence that inulin consists of fructofuranose units joined in the 1,2-positions.

Experiments on the comparative hydrolyses of these polysaccharides were carried out at 65 ± 0.2° using $N/10$ oxalic acid solution (B).

Experimental

The solutions were made up at 70° and rapidly transferred to the jacketed polarimeter tube. Corrections for the expansion of the glass, pipet and contained liquid were applied and all the results are calculated with the volumes reduced to 20°.

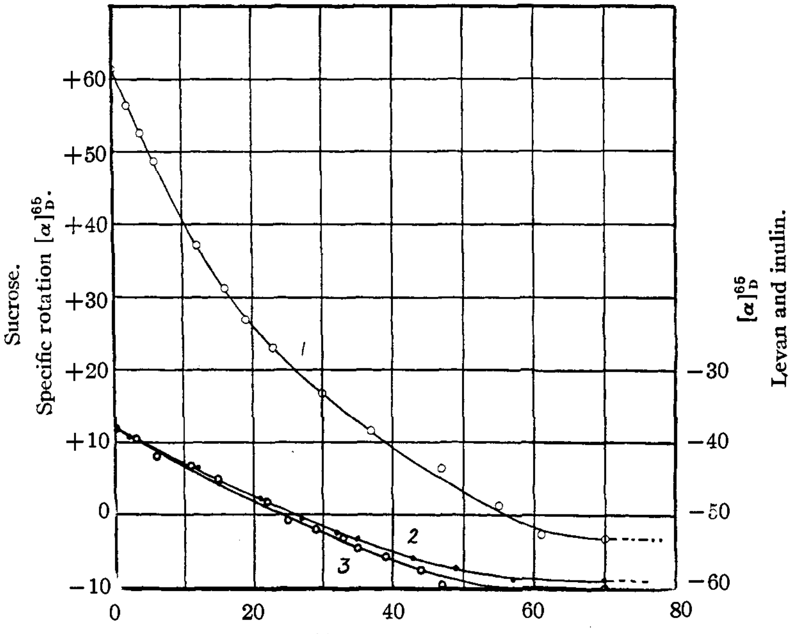

Fig. 2.—Rate of hydrolysis in N oxalic acid solution at 65°: 1, sucrose, ○; 2, inulin, ●; 3, levan, **o**.

The specific rotation of fructose at 65° may be calculated from the equation of Jungfleisch and Grimbert.[25]

$$[\alpha]^t_D = -[101.38 - 0.56t + 0.108(c - 10)]$$

where t is temperature in °C., and c is concentration in grams per 100 cc. Thus for a 1% solution at 65° $[\alpha]^{65}_D = -64.0$ in water; found, $[\alpha]^{65}_D$ −64.9 in solvent (B) for fructose.

The Hydrolysis of Inulin at 65°.—The results are given in Table VIII and plotted in Curve 2, Fig. 2.

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[25] Jungfleisch and Grimbert, *Compt. rend.*, 107, 390 (1888).

Table VIII

The Hydrolysis of Inulin at 65°

Concentration, 1.172 g. of inulin in 100 cc. of solvent (B)

Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$	Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$
0	−38.0	..	32	52.5	4.94
2	39.2	4.91	35	53.3	5.10
6	42.1	4.14	43	56.1	6.80
12	43.5	4.34	49	57.5	..
15	45.7	5.10	57	58.7	..
21	47.8	5.02	70	−58.7	..
27	50.5	4.75			

Mean value of $K = 5.01 \times 10^{-4}$. Final $[\alpha]^{25}_D = -80.0°$. Calcd. for inulin 100% fructose = −85.2°. % fructose from inulin = 94.0%.

The reaction does not appear to be monomolecular.

The Hydrolysis of Levan at 65°.—The results are given in Table IX and plotted in Curve 3, Fig. 2.

Table IX

The Hydrolysis of Levan at 65°

Concentration, 1.227 g. of levan in 100 cc. of solvent (B)

Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$	Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$
0	−38.0	..	29	52.1	5.99
3	39.4	3.64	33	53.3	6.00
6	41.9	5.42	35	54.6	6.68
11	43.2	4.08	39	55.9	7.18
15	45.2	4.40	44	57.7	8.56
22	48.3	4.77	47	59.7	..
25	50.8	5.72	52	60.0	..
			70	−60.0	..

Mean value of $K = 5.66 \times 10^{-4}$. $[\alpha]^{26}_D$ −83.0°. Calcd., −85.8°. % fructose from levan = 96.7%. The reaction is not monomolecular.

The Inversion of Cane Sugar at 65°.—The results are given in Table X and plotted in Curve 1, Fig. 2.

Table X

The Inversion of Cane Sugar at 65°

Concentration, 1.258 g. of sucrose in 100 cc. of solvent (B)

Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$	Time, min.	$[\alpha]^{65}_D$	$K \times 10^4$
0	+61.5	..	23	23.1	6.62
2	56.4	5.49	30	16.6	6.71
4	52.5	6.30	37	11.5	6.81
6	48.7	6.19	47	6.4	6.95
12	37.1	6.65	55	+1.3	..
16	31.3	6.63	61	−2.6	..
19	26.9	6.80	70	−2.6	..

Mean value of $K = 6.50 \times 10^{-4}$. These figures indicate a monomolecular reaction.

Discussion of Results

It is to be noticed that inulin yields only 94% while levan yields 97% of its weight as fructose according to the values of the specific rotations.

This has been noted repeatedly in the case of inulin and is attributed to a difructose anhydride by Jackson and Goergen.[26]

It appears that the three anhydrofructose derivatives studied hydrolyze under the experimental conditions at about the same speed. This is illustrated in Table XI, showing the mean velocity constants.

TABLE XI

MEAN HYDROLYSIS CONSTANT AT 65°

Substance	Sucrose	Levan	Inulin
$K \times 10^4$	6.50	5.66	5.01

The constants in the case of levan and inulin (Tables IX and X) indicate that the process is not monomolecular, since the values of K, in general, rise. They are sufficiently close, however, to indicate that these two polysaccharides belong to the same group of substances.

Summary

1. The rates of hydrolysis of cellulose, cellobiose, cellodextrin, starch, maltose and lactose, in a zinc chloride–hydrochloric acid solution, are compared at 23°.
2. It is concluded that the slow hydrolysis of cellulose is, in a large part, due to the slow hydrolysis of cellobiose; that cellobiose is not a reversion product, and that there seem to be no grounds to suppose that starch and cellulose are essentially different, except for the α-linkages in the former and the β-unions in the latter.
3. The rates of hydrolysis of sucrose, levan and inulin in 0.1 N oxalic acid solution at 65° have been measured.
4. It is established that these anhydrofructose derivatives hydrolyze at almost the same rate and it is concluded that this behavior is related to the γ-fructose residue present in each.
5. The technique developed is of possible application in the determination of the configurations of unknown polysaccharides.

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[26] Jackson and Goergen, *U. S. Bureau of Standards, Journ. Res.*, **3**, 28 (1929).