neutralized with the calculated quantity of a strong solution of potassium hydroxide (cooling) and rendered acid again with concentrated hydrochloric acid equivalent to exactly one-half the amount of the potassium hydroxide. The potassium acid salts of tartaric and racemic acids precipitate immediately and are filtered off after standing for forty-eight hours. The precipitate is washed with 60% alcohol.

The resulting precipitate is dried in the oven at 100° for twelve hours. A 1-g. sample is titrated with $N/5$ potassium hydroxide, then made up to 25 cc. and polarized. From the titration of pure potassium acid tartrate (26.58 cc.), and the specific rotation of potassium tartrate (α^{20}_{D} + 27.58°), the relative amounts of potassium acid tartrate and racemate may be calculated, together with inert material (potassium chloride). The weight of the equivalent potassium used in neutralizing is, of course, added to the original 1 g., in calculating the specific rotation of the unknown salt.

The filtrate from the potassium acid salts is evaporated to remove the alcohol, and sufficient calcium chloride added to be roughly equivalent to the oxalic acid as determined previously. This solution is immediately filtered hot and the filtrate neutralized. To this filtrate is added a solution equivalent to 5 g. of calcium chloride and allowed to crystallize for two days. The calcium trihydroxyxyloglutarate crystallizes rather slowly, and should only be filtered after no more crystals appear on the sides of the beaker after scraping down. The salt contains two molecules of water. It is not quite pure, but for purposes of analysis was considered as such because of the rather large loss on recrystallization: CaO determined, 21.87%; calcd. 22.06%. The free acid obtained by breaking up the salt with oxalic acid has no polarization and readily crystallizes from water; it melts at 142–144° and titrates 55.1 cc. of $^1/_5N$ KOH, calcd. 55.5.

Summary

1. The probable mechanism of the breakdown of 5-keto-gluconic acid on oxidation with nitric acid in the presence of vanadium is shown.

2. The application of the method as a means for the study of the oxidation of other carbohydrate derivatives is suggested.

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Solubility of Inulin

BY E. YANOVSKY AND R. M. KINGSBURY

Such expressions as "insoluble" and "slightly soluble" applied to inulin are very common in the literature, but actual measurements recorded are very few. Some of the old fragmentary results on solubility of inulin in water and alcoholic solutions are recorded by Dragendorff,[1] von Lippmann,[2] and Prantl.[3] Wolff and Geslin[4] investigated the comparative solubilities of inulin from chicory and dahlia with the results in Table I.

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(1) Dragendorff, "Materialien zu einer Monographie des Inulins," St. Petersburg, 1870, pp. 54 and 66.

(2) Von Lippmann, "Chemie der Zuckerarten," 1904, p. 797.

(3) Prantl, "Das Inulin," München, 1870, p. 21.

(4) Wolff and Geslin, *Bull. soc. chim. biol.*, **2**, 19 (1920).

TABLE I

t, °C.			15	30	40	45	50
Soly., grams in 100 cc.	Inulin from dahlia	I	0.045	0.185	0.305	...	0.558
		II	.333	.575	.920	...	1.490
	Inulin from chicory	I	.225	.400	.975	1.160	1.737
		II	1.445	1.859	2.400	...	...

The first line in each case represents inulin crystallized from water, the second, inulin precipitated with alcohol. Crystallization with the aid of alcohol increases the solubility of both; the chicory inulin, however, still remains the more soluble. Somewhat more detailed data on the solubility of inulin are presented in the following pages.

Materials Used.—Inulin was prepared from dahlia roots and chicory roots by the usual method[5] of extracting the roots with hot water, treating the solution with neutral lead acetate, removing the excess of lead with hydrogen sulfide, and evaporating the solution to the crystallization point. The inulin thus obtained was recrystallized four times by dissolving in hot water, treating with decolorizing carbon, and precipitating with alcohol. The final products, as used in the experiments described below, were white powders. Cursory microscopic examination showed that chicory inulin was the more crystalline of the two, consisting almost entirely of the typical spherocrystals, whereas dahlia inulin appeared to be largely amorphous with a few spherocrystals here and there. The specific rotation of dahlia inulin was found to be $[\alpha]^{20}_{D}$ −36.9°; that of chicory inulin was $[\alpha]^{20}_{D}$ −34.6°. Dahlia inulin contained 0.06% ash, chicory inulin contained 0.12%. Dahlia inulin had 0.45% reducing sugar, chicory inulin had 0.55%.

Analytical Procedure.—In analyzing inulin, or mixtures of inulin and levulose, two factors must be considered. First, that inulin is not hydrolyzed completely with acids at room temperature,[6] and second, that levulose gradually decomposes on heating with acids. The procedure used was as follows: a number of solutions of carefully purified inulin and levulose were brought to 99–100° (in boiling water). To 20 cc. of solution 5 cc. of 2.313 *N* hydrochloric acid was added. At frequent intervals (from one minute up) solutions were taken out, cooled quickly in ice water, neutralized, and brought to definite volume. Reducing sugar was determined by the Munson and Walker method. From several series of determinations it was found that heating for fifteen to sixteen minutes is sufficient to hydrolyze all the inulin; the correction for levulose decomposed is 3.0%.

In converting glucose values from the Munson and Walker tables into levulose a uniform factor 0.915 was used, thus admittedly introducing a small, for our purposes, rather negligible, error.[7] Likewise no correction has been made for glucose found by several investigators[6,8] after acid hydrolysis of inulin but apparently not formed (or formed only in small quantities) on hydrolysis by inulase.[9]

In view of the fact that the values for cuprous oxide in some of our results were very low the Fehling solution used was checked several times during the progress of experiments, but at no time did a blank determination with 50 cc. of water give more than one milligram of cuprous oxide.

Solubility of Inulin in Water at 20°.—Mixtures of water and inulin were kept at

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(5) Woskressensky, *J. prakt. Chem.*, **37**, 309 (1846).

(6) Jackson and Goergen, *Bur. Standards J. Research*, **3**, 27 (1929).

(7) Browne, THIS JOURNAL, **28**, 439 (1906); Jackson and Mathews, *Bur. Standards J. Research*, **8**, 403 (1932).

(8) Tanret, *Bull. soc. chim.*, **9**, 200, 227, 622 (1893); Schlubach and Elsner, *Ber.*, **62**, 1493 (1929).

(9) Bourquelot and Bridel, *Compt. rend.*, **172**, 946 (1921); Pringsheim and Ohlmeyer, *Ber.*, **65**, 1242 (1932).

20 ± 1° in tightly stoppered flasks and shaken by hand several times each day. Samples were removed at intervals of several days, filtered, and analyzed for reducing sugars and inulin. The results, given in Table II, indicate clearly that there is a substantial difference in the solubility of dahlia and chicory inulins, the latter being considerably more soluble. The findings corroborate the results of Wolff and Geslin, although their actual figures are somewhat different from ours. The most interesting fact brought out is that, although the solubility of dahlia inulin remained apparently constant during the period of experiment, the chicory inulin showed a very gradual but decided decrease in solubility.

TABLE II

SOLUBILITY OF INULIN AT 20 ± 1° IN GRAMS PER 100 CC.

Time, days	Dahlia inulin		Chicory inulin		Time, days	Chicory inulin	
	Expt. I	Expt. II	Expt. I	Expt. II		Expt. I	Expt. II
1	0.16	..	1.48	..	23	1.02	...
5	..	0.16	..	1.21	27	0.85	...
9	0.16	..	1.20	..	29		0.91
10	..	0.18	..	..	35		.94
13	..	..	..	1.09	40		.85
14	..	..	1.19	..	47		.80
20	0.16	0.15	1.00	1.01	54		.76

In the figures given above no correction has been made for the small amounts of reducing sugar found; there was no increase in reducing sugar during the course of the experiment. This statement applies to all subsequent results, unless otherwise stated. The rather low values for dahlia inulin solubility were checked by evaporating the solutions and drying *in vacuo* to constant weight. Two results (0.16 and 0.16) agreed well with those given in the table.

Since the results in Table II were obtained with inulin recrystallized with the aid of alcohol, and Wolff and Geslin obtained different results when inulin was recrystallized from water, we made similar experiments. Pure chicory inulin was recrystallized three times from water without the aid of alcohol. This inulin was soluble to the extent of 0.12 g. per 100 cc., and the value for solubility did not change during six weeks' observation. In a duplicate experiment a value of 0.13 g. per 100 cc. was obtained. The figures for similarly treated dahlia inulin were: 0.03 and 0.04 g. per 100 cc.

It appears therefore that there are two forms of inulin of entirely different degrees of solubility, and that the two forms of chicory inulin are different from the corresponding forms of dahlia inulin. The form of chicory inulin obtained by the usual method of recrystallization with the aid of alcohol seems to be the unstable modification, which gradually changes into the less soluble form.

That the stable less soluble modification of chicory inulin can be transformed into the unstable more soluble modification was shown by the following experiments. Chicory inulin having an unchanging solubility of 0.12 g. per 100 cc. was recrystallized (1) from water with an equal volume of alcohol added, and (2) from the same amount of water with four volumes of alcohol added. The solubility of the first product was found to be 0.52 g. per 100 cc., but it gradually decreased to 0.32 g.; the solubility of the second product was 1.17 g. per 100 cc. after four days, and this decreased gradually to 0.40 g.

Solubility at Other Temperatures.—Table III gives the results on solubility of inulin at 6°. The figures for dahlia inulin approach the limits of the accuracy of the method. The values for chicory inulin show a gradual decrease, but not as prominent, as was noted at 20°.

The data in Table IV show that at 39° the solubility of chicory inulin decreases in a shorter time than at 20°. The solubility of dahlia inulin remained stationary.

TABLE III

SOLUBILITY OF INULIN AT 6 ± 1°, IN G. PER 100 CC.

Time, days	Dahlia inulin Expt. I	Dahlia inulin Expt. II	Chicory inulin Expt. I	Chicory inulin Expt. II
6	0.08	0.08	0.58	0.60
15	.02	.03	.52	.54
21	.02	.02	.51	.54
26	...	...	.49	.50

At this temperature a gradual increase in reducing sugar was noticed, and the figures of the table were corrected accordingly. The corrections were: for dahlia inulin, 0.17, 0.24 and 0.31; for chicory inulin, 0.33, 0.51 and 0.74.

TABLE IV

SOLUBILITY OF INULIN AT 39 ± 1°, IN G. PER 100 CC.

Time, days	Dahlia inulin Expt. I	Dahlia inulin Expt. II	Chicory inulin Expt. I	Chicory inulin Expt. II
5	0.55	0.50	4.08	4.39
8	.48	.57	3.80	3.73
12	.50	.48	3.00	3.28

Solubility in 50% Alcohol.—The usual laboratory procedure in the preparation of inulin requires precipitation of a water solution of inulin with alcohol. Knowledge of the solubility of inulin in alcoholic solutions is therefore of interest. Table V shows that only traces of dahlia inulin are dissolved in 50% alcohol. The gradual decrease in solubility of chicory inulin is not pronounced. The last column of the table represents results obtained by evaporating the solutions and drying to constant weight.

TABLE V

SOLUBILITY OF INULIN IN 50% ALCOHOL AT 20 ± 1°, IN G. PER 100 CC.

Time, days		5	9	10	20	22	23
Dahlia inulin	Expt. I	0.06	0.04	..	0.03	..	(0.04)
	Expt. II	.04	..	0.04	.03	..	(.04)
Chicory inulin	Expt. I	.11	.15	..	.11	.07	(.07)
	Expt. II	.11	..	.12	.06	.07	(.07)

Solubility in Presence of Levulose.—In nature inulin is always accompanied by variable amounts of free levulose. We have investigated the solubility of inulin in solu-

TABLE VI

SOLUBILITY OF INULIN IN PRESENCE OF LEVULOSE AT 20 ± 1°, IN G. PER 100 CC.

Concn. of levulose in solvent	Dahlia inulin Levulose found	Dahlia inulin Inulin found	Chicory inulin Levulose found	Chicory inulin Inulin found
0.00	0.02	0.16	0.03	1.20
.24	..	..	.25	0.91
.49	..	..	.46	1.11
.96	0.95	.18	.92	1.09
1.91	..	..	1.90	1.00
2.84	2.90	.19	2.84	0.99
4.69	4.71	.23	4.74	1.05
9.11	9.18	.41	9.09	1.10
13.31	13.54	(.22)	13.31	1.08
17.27	17.30	.62	17.17	1.06
24.56	24.42	.94	23.80	1.37

tions of different concentrations of levulose, and the results are given in Table VI. It appears that the solubility of dahlia inulin gradually increases with the increase of levulose in solution. In 25% levulose solution the solubility of dahlia inulin is practically equal to that of chicory inulin. On the other hand, the presence of levulose (up to 25%) does not seem to affect the solubility of chicory inulin.

Solubility in Presence of Soluble Inulin.—The yield of inulin prepared from a plant is considerably below the amount present in the plant as determined analytically. The uncrystallizable material represents either the degradation products of inulin or some form of soluble inulin. Therefore, we measured the solubility of inulin in solutions of soluble inulin prepared from camas bulbs.[10] The results given in Table VII show that the soluble inulin under the conditions observed is without any effect upon the solubility of either dahlia or chicory inulin.

TABLE VII

SOLUBILITY OF INULIN IN PRESENCE OF SOLUBLE INULIN AT 20 ± 1°, IN G. PER 100 CC.

Time, days	1	5	9	10	14	20
Control soln. of soluble inulin	1.33	1.37	1.31	1.33	1.33	1.32
Dahlia inulin	..	0.12	0.11	0.16	..	0.16
Chicory inulin	..	1.29	1.23	..	1.10	.97

Separation of Inulin from Supersaturated Solutions.—In common with other carbohydrates inulin easily forms supersaturated solutions. The knowledge of the extent of separation of inulin from its supersaturated solution is, of course, of utmost importance in the preparation of inulin. The existence of supersaturated solutions of inulin was known to early investigators.[1] Kiliani[11] noticed that if inulin is dissolved at higher temperature and then cooled, more inulin remains in solution than one would expect from the solubility data. Similar observation had been made by Tanret.[8] No data, however, were given by either investigator. We took a mixture of inulin and water, and after slightly warming it to produce a supersaturated condition kept the mixture at 20°. The supersaturated solution of dahlia inulin with an initial concentration of about ten times its normal solubility gradually deposited inulin, but it did not reach the normal solubility during the seven weeks of observation (Table VIII). The solution of chicory inulin, which had initially about twice the normal solubility, reached its solubility level at 20° in three to four weeks' time.

TABLE VIII

SUPERSATURATED SOLUTIONS OF INULIN IN WATER AT 20 ± 1°, IN G. PER 100 CC.

	Dahlia inulin		Chicory inulin	
Time, days	Expt. I	Expt. II	Expt. I	Expt. II
1	1.60	..	2.24	..
5	..	1.13	..	1.92
9	1.04	..	1.81	..
10	..	0.99	..	1.74
14	0.93	.90	1.68	1.65
24	.72	.73	1.41	1.43
35	.69	.67	1.20	1.12
42	.61	.59	1.08	1.05

In another experiment with chicory inulin we used the mother liquor from recrystallization of inulin. Pure inulin was dissolved in boiling water, and the solution kept overnight in a refrigerator. The separated inulin was filtered off next day. The mother liquor, which contained 5.83% inulin, was kept at 20°. The gradual decrease in concen-

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(10) Yanovsky and Kingsbury, THIS JOURNAL, **53**, 1597 (1931).

(11) Kiliani, *Liebigs Ann. Chem.*, **205**, 145 (1880).

tration of inulin in solution is shown in Table IX. The level of solubility at 20° was reached in four to five weeks.

TABLE IX

SEPARATION OF CHICORY INULIN FROM ITS SUPERSATURATED SOLUTION

Time, days	0	5	12	23	28	36
Inulin per 100 cc. of soln., g.	5.83	3.97	2.18	1.65	1.49	1.34

Summary

The solubility of dahlia inulin differs considerably from that of chicory inulin. Each of the two inulins exists in two modifications having different degrees of solubility. One of the modifications of chicory inulin is unstable, gradually changing into the less soluble form. Solubility was measured at different temperatures and in alcoholic solutions. The presence of levulose increases the solubility of dahlia inulin, but has no effect on the solubility of chicory inulin. Soluble inulin has no effect on the solubility of either dahlia or chicory inulin. Inulin is slowly deposited from its supersaturated solutions until normal solubility is reached.

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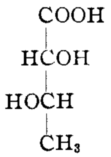
[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

The C_4-Saccharinic Acids. VII. The Preparation and Resolution of *dl-threo*-1,2-Dihydroxybutyric Acid[1]

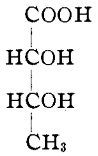
BY J. W. E. GLATTFELD AND JOHN W. CHITTUM

There are two theoretically possible *dl*-1,2-dihydroxybutyric acids. Both of these have recently been prepared in pure form and studied quite thoroughly.[2] One melts at 74–75° and the other at 81.5°. In still more recent work in this Laboratory[3] it has been shown that the acid of lower melting point probably has the *trans* configuration and the one of higher melting point the *cis* configuration. Braun has suggested the prefix *threo* for the *trans* acid and *erythro* for the *cis* acid. These suggestions are adopted in this paper.



$$\begin{array}{c} COOH \\ | \\ HCOH \\ | \\ HOCH \\ | \\ CH_3 \end{array}$$

dl-threo-1,2-Dihydroxybutyric acid, m. p. 74–75°



$$\begin{array}{c} COOH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ CH_3 \end{array}$$

dl-erythro-1,2-Dihydroxybutyric acid, m. p. 81.5°

It is with the *dl-threo*-acid that this paper is concerned.

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[1] This article is largely from a dissertation presented by John W. Chittum in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

[2] Glattfeld and Woodruff, THIS JOURNAL, **49**, 2309 (1927).

[3] Géza Braun, *ibid.*, **51**, 228 (1929).