The amylase activities were all measured under the same specified conditions[5] with 1% soluble potato starch adjusted to 0.02 *M* sodium chloride, 0.01 *M* phosphate and *p*H 7.2.[5] The saccharogenic activity refers to the increase in the reducing value (calculated as maltose) of the reaction mixture in thirty minutes at 40° brought about by one milligram of the enzyme preparation when the concentrations of the amylase were selected to give approximately the same (20%) hydrolysis of the starch.

Results

A number of reagents which have been reported to be specific for free sulfhydryl groups[6] were studied for their influence upon the activity of pancreatic amylase. Typical data are summarized in Table I. These results show that the reagents studied had little if any influence upon the activity of pancreatic amylase and lead to the conclusion that free sulfhydryl groups are of little if any importance to the activity of this amylase.

This finding with pancreatic amylase is in marked contrast to the results obtained under similar conditions with these reagents with β-amylase from barley and from malted barley.[3b] In this case, these sulfhydryl reagents caused complete inactivation of the amylase. Moreover, it was possible to restore the amylase activity by treatment of the inactivated enzyme solutions with hydrogen sulfide or with cysteine, a confirmation of the conclusion that sulfhydryl groups are essential to β-amylase activity.

In addition, it is interesting to note that the highly active solutions of pancreatic amylase used here gave no evidence of the presence of free sulfhydryl groups when examined by the nitro prusside reaction, as modified by Anson.[7] This finding is in accord with previous more qualitative indications[2a] and is again in marked contrast to the observations with beta-amylase from barley and from malted barley. With this enzyme, the amylase activities of the solutions were found to be directly proportional to the concentrations of sulfhydryl.[3b,7]

TABLE I

A STUDY OF THE INFLUENCE OF SPECIFIC SULFHYDRYL REAGENTS UPON THE ACTIVITY OF PANCREATIC AMYLASE

Treatment		After treatment Activity	
Reagent	Concn., *M*	Units[d]	% of control
Phenylmercuric-chloride[a]	0	5,200	100
	(satd. soln.)	4,920	95
p-Chloromercuri-benzoic acid[b]	0	5,400	100
	0.0005	4,870	90
Iodoacetamide[c]	0	6,150	100
	0.05	6,350	103

[a] Amylase solutions adjusted to 0.1 *M* phosphate; *p*H 6.8, reacted with reagent for thirty minutes at 0°.

[b] Amylase solutions adjusted to 0.1 *M* phosphate; *p*H 7.0, reacted with reagent for thirty minutes at 0°.

[c] Amylase solutions were adjusted to 0.1 *M* phosphate; *p*H 6.8, treated with the reagent and held at 25° for 120 minutes. The control was treated in the same way except that no iodoacetamide was added.

[d] Milligrams of "maltose" formed in thirty minutes at 40° by one milligram of enzyme acting on 1% soluble potato starch at *p*H 7.2 in the presence of 0.01 *M* phosphate and 0.02 *M* sodium chloride.

Summary

The data presented here confirm and extend previous indications that sulfhydryl groups of the protein are not essential to the activity of pancreatic amylase.

They emphasize another difference between the two typical starch-splitting enzymes, pancreatic amylase and β-amylase from barley and from malted barley.

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(5) H. C. Sherman, M. L. Caldwell and M. Adams, THIS JOURNAL, **50**, 2529, 2535, 2538 (1938).

(6) L. Hellerman and M. E. Perkins, *J. Biol. Chem.*, **107**, 241 (1934); E. D. Schock, J. Jensen and L. Hellerman, *ibid.*, **111**, 553 (1935); L. Hellerman and M. E. Perkins, *ibid.*, **112**, 175 (1935-6); L. Hellerman, *Physiol. Rev.*, **17**, 454 (1937); L. Hellerman, F. P. Chinard and V. R. Dietz, *J. Biol. Chem.*, **147**, 443 (1943).

(7) M. L. Anson, *J. Gen. Physiol.*, **24**, 399 (1940-1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

A New Synthesis of Methyl 3,4,6-Trimethyl-β-D-glucoside and the Preparation of Crystalline 3,4,6-Trimethyl-D-glucose

BY ROBERT L. SUNDBERG, CHESTER M. MCCLOSKEY, DONALD E. REES AND GEORGE H. COLEMAN

In 1934 Haworth, Hirst and Panizzon[1] reported the synthesis of 3,4,6-trimethyl-D-glucose. This represented the synthesis of the last of the four possible trimethyl-D-glucopyranoses which are so important in the determination of the structures of oligo- and polysaccharides. Two of the four have previously been reported as crystalline, 2,3,6-trimethyl-D-glucose[2] and 2,4,6-trimethyl-D-glucose.[3]

(1) Haworth, Hirst and Panizzon, *J. Chem. Soc.*, 154 (1934).

(2) Irvine and Hirst, *ibid.*, 1213 (1922).

(3) Haworth and Sedgwick, *ibid.*, 2573 (1926).

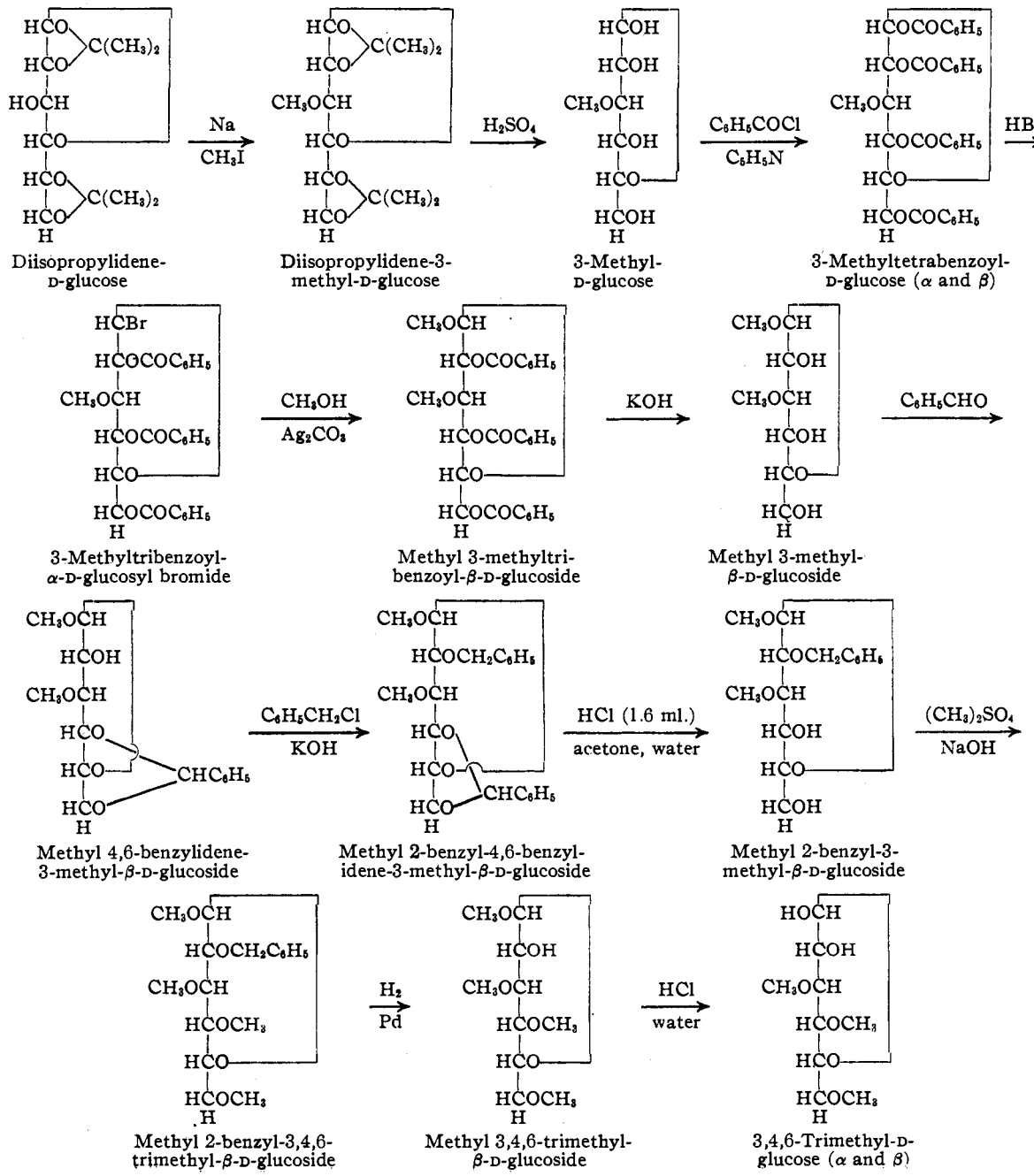
A sample of 3,4,6-trimethyl-D-glucose which had been prepared in this Laboratory by the hydrolysis of methyl 3,4,6-trimethyl-β-D-glucoside crystallized spontaneously on standing. This leaves, therefore, 2,3,4-trimethyl-D-glucose as the only one of the four which has not been obtained crystalline.

Samples of 3,4,6-trimethyl-D-glucose subsequently prepared in this Laboratory by the same method crystallized readily at room temperature. The crystals were thick plates (m. p. 97–98° (cor.) after recrystallization) and proved to be the

beta isomer, which is considerably less soluble in isopropyl ether than the alpha form. The filtrate from the beta crystals was cooled in the refrigerator, and crystalline material obtained in which the alpha form (needles) predominated. The melting point of this product was 64–67° (cor.). Several recrystallizations from isopropyl ether with cooling raised the melting point to 76–77° (cor.).

It should be noted in this connection that the first small sample of 3,4,6-trimethyl-D-glucose which crystallized (needles) had a melting point after two recrystallizations of 78–80°. The melting point did not change on further recrystallization. It, therefore, seems probable that this was the alpha isomer. In the samples of this compound which have been prepared subsequently, the beta form has crystallized first.

That the thick plates were the beta form was indicated by the rise in specific rotation from 41.1 to 78° at equilibrium. Another sample of these crystals had a specific rotation of 77.5° immediately after dissolving in water containing a trace of ammonia. That the needle crystals



were the alpha form was shown by the change in specific rotation from 91.9 to 77.4° at equilibrium.

The methyl 3,4,6-trimethyl-β-D-glucoside, from which the trimethyl-D-glucose was prepared, was obtained by a new synthesis. This compound was first prepared by Haworth, Hirst and Panizzon[1] from "Brigl's" anhydride. The procedure involved the action of methyl alcohol on the anhydride, tosylation of methyl 3,4,6-triacetyl-β-D-glucoside, deacetylation, methylation, and finally a long ammonolysis at high temperature in methyl alcohol of the methyl 2-tosyl-3,4,6-trimethyl-β-D-glucoside to give the desired product.

The new synthesis involved the preparation of methyl 3-methyl-β-D-glucoside from 3-methyl-D-glucose. The benzylidene derivative[4] was then prepared, which on benzylation in the 2-position and subsequent removal of the benzylidene radical by mild acid hydrolysis, formed methyl 2-benzyl-3-methyl-β-D-glucoside. Methylation of this compound and reduction to remove the benzyl radical gave methyl 3,4,6-trimethyl-β-D-glucoside. The various steps in this synthesis from diisopropylidene-D-glucose are shown in the accompanying equations.

In the preparation of methyl 3-methyl-β-D-glucoside the small-scale method of Oldham[5] was adapted to large scale procedure. This method, which involves the benzoylglucosyl bromide, was used rather than the acetylglucosyl bromide method of Helferich and Lang[6] since considerably higher yields are obtained. Difficulty was encountered in the complete removal of the benzoyl groups using potassium methylate as described by Oldham, and subsequent treatment with aqueous potassium hydroxide was necessary to effect complete removal. The incompletely debenzoylated compound crystallized readily and was soluble in warm water, suggesting that only one benzoyl group remained. It is very possible that it is located in the number two position since Helferich and Lang encountered similar difficulty with the deacetylation of the corresponding acetyl compound and obtained the 2-acetyl derivative of both the methyl and phenyl 3-methyl-β-D-glucosides. McCloskey and Coleman[7] also found that potassium methylate alone would not remove all of the benzoyl groups of phenyl 3-methyltribenzoyl-β-D-glucoside.

By the use of methyl iodide and silver oxide as reagents, direct methylation of the monobenzoyl derivative (assuming that it was the 2-benzoyl derivative) to give the trimethyl glucoside was a possibility. The longer route was chosen, however, as it was surer and more exact structurally. It also permitted the use of methyl sulfate and alkali as methylating reagents.

Since methyl 3-methyl-β-D-glucoside is not obtained crystalline, it was not isolated but converted directly to its 4,6-benzylidene derivative. Although this compound and subsequent ones are all easily crystallized, it was found that a much higher over-all yield was obtained if purification was not carried out until the isolation of methyl 2-benzyl-3-methyl-β-D-glucoside.

With the exception of the preparation of methyl 3-methyl-β-D-glucoside, the steps are all simple and give good yields. The synthesis involves a total of eleven steps. The over-all yield from diisopropylidene-D-glucose to methyl 3,4,6-trimethyl-β-D-glucoside was 9.4%, which is equivalent to an average yield of a little better than 80% in each step.

Experimental

3-Methyl-D-glucose.[8]—To a solution of 300 g. of diisopropylidene-D-glucose in 900 ml. of dry ether was added 30 g. of sodium cut in pieces about the size of a pea. The reaction mixture was protected from moisture by the use of a calcium chloride drying tube. As soon as the initial vigorous reaction had subsided, 10 g. of fine sodium wire was added and the mixture allowed to stand for twenty-four hours. The excess sodium was removed, 150 g. of methyl iodide added, and the solution refluxed for about seven hours on a steam-bath. After cooling to room temperature a few milliliters of water was added, and after separating the aqueous sodium iodide layer the ether was removed by distillation. One hundred and fifty milliliters of toluene was added and then removed by distillation under reduced pressure to dry the solution. An equal volume of dry ether was added and the above methylation repeated using methyl iodide in proportion to the amount of sodium dissolved. The ether was distilled off and the residue added to six liters of water containing 120 ml. of concentrated sulfuric acid. The mixture was stirred on a steam-bath for two hours, neutralized with an excess of barium carbonate, filtered, and the solid precipitate washed with water. The solution was concentrated under reduced pressure to about 2 liters, treated with charcoal, filtered, and evaporated to a thick sirup under reduced pressure. An equal volume of methyl alcohol was added and the mixture warmed with stirring until it became homogeneous. One-tenth the volume of acetone was added slowly and the solution set aside to crystallize. After twenty-four hours the crystals were filtered off and the filtrate concentrated and reworked. A total yield of 150–180 g. (46–56%) of crude product was obtained.

3-Methyltetrabenzoyl-D-glucose.—To a solution of 75 g. of 3-methyl-D-glucose in 285 ml. of anhydrous pyridine was added slowly 235 ml. of benzoyl chloride while cooling the flask in a water-bath. After the benzoyl chloride had all been added, the mixture was placed in an oven at 60° for two hours and then allowed to stand at room temperature overnight. The following day the solid was triturated with sufficient water to decompose the excess benzoyl chloride. The mixture was extracted with 1.5 liters of chloroform followed by 0.5 liter of water. The aqueous extract was extracted with 0.5 liter of chloroform and the chloroform extracts combined. The chloroform solution was washed successively with 0.5 liter of 20% hydrochloric acid, 0.5 liter of 4 *N* sodium hydroxide, and 0.5 liter of water. The chloroform was removed by distillation on a steam-bath, finishing under reduced pressure. The residue was broken up and beaten to a thin slush by mechanical stirring with 0.5 liter of hot methyl alcohol. The mixture was cooled to room temperature, filtered, the solid washed with methyl alcohol, and air dried. The yield of crude α,β-mixture was 184 g. (78%).

Methyl 3-Methyltribenzoyl-β-D-glucoside.—A solution of 500 g. of 3-methyltetrabenzoyl-D-glucose in 2.75 liters of

(4) Freudenberg, Toepffer and Anderson, *Ber.*, **61**, 1758 (1928).

(5) Oldham, THIS JOURNAL, **56**, 1360 (1934).

(6) Helferich and Lang, *J. prakt. Chem.*, (2) **132**, 321 (1932).

(7) McCloskey and Coleman, *J. Org. Chem.*, in press.

(8) Loder and Lewis, THIS JOURNAL, **54**, 1044 (1932); Schmidt and Simon, *J. prakt. Chem.*, **152**, 195 (1939).

dry benzene, 1 liter of glacial acetic acid saturated at 0° with anhydrous hydrogen bromide, and 0.75 liter of anhydrous ether was allowed to stand at room temperature overnight. The solution was then mixed with ice and water, and the non-aqueous layer extracted twice with ice water and once with a saturated potassium bicarbonate solution. The non-aqueous layer was dried over powdered calcium chloride, filtered, and one-half its volume of absolute methyl alcohol and 200 g. of silver carbonate added. The mixture was stirred for forty-eight hours and then heated to reflux for three hours. After filtering off the silver salts the solution was evaporated nearly to dryness, transferred to large evaporating dishes, and allowed to evaporate to dryness in the air.

Methyl 4,6-Benzylidene-3-methyl-β-D-glucoside.—The crude methyl 3-methyltribenzoyl-β-D-glucoside (350–400 g.) was dissolved in 2.5 liters of hot absolute methyl alcohol, and to the solution was added a solution of 8 g. of potassium in 80 ml. of methyl alcohol. The solution was heated to boiling, kept at this temperature for about one minute, and 4 liters of water then added. The solution was concentrated under reduced pressure until no more methyl benzoate distilled over, and then 120 g. of potassium hydroxide was added and the solution left at room temperature overnight. The following morning the solution was acidified with dilute sulfuric acid until just acid to phenol blue. The benzoic acid which crystallized was filtered off and the filtrate extracted with 500 ml. of ether. The aqueous solution was made alkaline to phenol-blue with a little potassium hydroxide solution and concentrated to dryness under reduced pressure. About 500 ml. of toluene was added and then distilled under reduced pressure to remove the last of the alcohol. The residue was triturated with 100 ml. of warm benzaldehyde until a homogeneous mixture was obtained. An additional 550 ml. of benzaldehyde and 400 g. of powdered anhydrous zinc chloride were added and the mixture shaken vigorously for twelve hours. The reaction mixture was poured into a large beaker and sufficient water added with stirring to dissolve the zinc chloride. To this was added with stirring, 1.5 volumes of ligroin (30°). The crystals which formed were filtered off, washed with water and ligroin, and dried in the air. The product as such was sufficiently pure for the next step. The yields of crude material were from 135–150 g. (56–62%) based on 3-methyltetrabenzoyl-D-glucose. Absolute alcohol is a good solvent for recrystallization. However, it was found that a higher over-all yield was obtained without purification at this point.

Methyl 2-Benzyl-4,6-benzylidene-3-methyl-β-D-glucoside.—A mixture of 140 g. of crude methyl 4,6-benzylidene-3-methyl-β-D-glucoside, 140 g. of powdered potassium hydroxide, and 910 ml. of benzyl chloride was stirred on a steam-bath for five hours. Most of the excess benzyl chloride was distilled off under reduced pressure, water was added, and the remaining benzyl chloride removed by steam distillation. The glucoside usually solidified during the steam distillation. The mixture was cooled to room temperature and the solid filtered off. The dry solid weighed 132 g. (72%). The pure compound was obtained as long needles by crystallization of 50 g. from a mixture of 250 ml. of acetone and 50 ml. of water: m. p. 147–148° (cor.), $[\alpha]^{25}D$ −30.3° (*c* = 2, U. S. P. chloroform).

The compound is very soluble in chloroform; soluble in dioxane, hot ethyl acetate, and hot benzene; moderately soluble in acetone and ethyl acetate; and sparingly soluble in benzene, hot ethanol, and hot ligroin (60°).

Anal. Calcd. for $C_{23}H_{26}O_6$: C, 68.36; H, 6.78. Found: C, 68.29; H, 6.8.

Methyl 2-Benzyl-3-methyl-β-D-glucoside.—To a hot solution of 130 g. of crude methyl 2-benzyl-4,6-benzylidene-3-methyl-β-D-glucoside in 1.3 liters of acetone was added a solution of 133 ml. of water and 1.6 ml. of concentrated hydrochloric acid. The mixture was maintained at gentle reflux for four hours and neutralized with an excess of potassium bicarbonate. The acetone was largely removed under reduced pressure and 1.3 liters of water added. The mixture was distilled under reduced pressure as long as benzaldehyde came over. This required the distillation of one-half to two-thirds of the original volume. The solution was filtered to remove solid material and concentrated to dryness under reduced pressure. One liter of toluene was added and the solution again concentrated under reduced pressure on a steam-bath until the volume was approximately 500 ml. Any solid material was filtered off and the filtrate set aside to crystallize. The yield was 69 g. (68%). Recrystallization of the product from toluene formed needles, m. p. 102.5–103° (cor.); $[\alpha]^{25}D$ −5.8° (*c* = 2, C. P. acetone).

The compound is soluble in chloroform, acetone, and dioxane; moderately soluble in ethanol, ethyl acetate, and hot benzene; slightly soluble in benzene; and very slightly soluble in hot ligroin (60°).

When pure methyl 2-benzyl-4,6-benzylidene-3-methyl-β-D-glucoside was used as starting material instead of the crude, 14 g. (90%) of product was obtained from 20 g. of the glucoside. It was found advantageous, however, to use the crude material as described.

Anal. Calcd. for $C_{14}H_{22}O_6$: C, 58.73; H, 7.75. Found: C, 60.43; H, 7.60.

Methyl 2-Benzyl-3,4,6-trimethyl-β-D-glucoside.—The methylation of 120 g. of methyl 2-benzyl-3-methyl-β-D-glucoside was carried out in 500 ml. of acetone at 50° by the simultaneous dropwise addition of 315 ml. of methyl sulfate and 350 ml. of 50% sodium hydroxide solution. The flask was equipped with a mechanical stirrer and distillation tube connected to a condenser. The rate of addition of reagents was regulated so that the acetone distilled slowly. When all reagents had been added, the temperature of the solution was raised and kept at 70° for an hour. The reaction mixture was diluted with 1.5 liters of water, cooled to room temperature, and extracted twice with an equal volume of chloroform. The chloroform solution was distilled until nearly all the solvent had been removed, toluene was added and removed under reduced pressure. The methylation procedure was then repeated, but the second time the residue was not treated with toluene but fractionally distilled through a platinum packed column; b. p. 125° (0.008 mm.). The distillate crystallized on standing. It was recrystallized from ligroin (30°) by cooling to −15° in the refrigerator and formed thick needles. The yield was 115 g. (88%), m. p. 41.5–42°, $[\alpha]^{25}D$ 9.9° (*c* = 2, U. S. P. chloroform).

Anal. Calcd. for $C_{16}H_{26}O_6$: C, 61.12; H, 8.32. Found: C, 62.61; H, 8.05.

Methyl 3,4,6-Trimethyl-β-D-glucoside.—To a solution of 19 g. of methyl 2-benzyl-3,4,6-trimethyl-β-D-glucoside in 50 ml. of glacial acetic acid was added 0.5 g. of palladiumized charcoal. The mixture was shaken under hydrogen (40 lb. pressure) for twenty-four hours, during which time one mole equivalent of hydrogen was absorbed. The solution was filtered and the residue washed with water. The filtrate and washings were concentrated under reduced pressure to a sirup; then 50 ml. of water was added and the solution concentrated again. Finally after 200 ml. of toluene had been added and removed under reduced pressure, the residue was dissolved in 150 ml. of ligroin (60°) containing a few drops of chloroform. On standing crystals of methyl 3,4,6-trimethyl-β-D-glucoside formed. The yield was 12.5 g. (92.5%) of material sufficiently pure for the following hydrolysis. After recrystallization the melting point was 51.5–52.5° (cor.); $[\alpha]^{25}D$ −16.4° (*c* = 2, U. S. P. chloroform[9]).

3,4,6-Trimethyl-D-glucose.—A solution of 12 g. of methyl 3,4,6-trimethyl-β-D-glucoside in 400 ml. of aqueous 5% hydrogen chloride was refluxed for two and one-half hours. When the solution had cooled, it was neutralized with silver carbonate, the silver salts filtered off, and the

(9) Haworth, Hirst and Panizzon, *J. Chem. Soc.*, 154 (1934), m. p. 51°; $[\alpha]^{20}D$ −20° (*c* = 1.1 chloroform); Peat and Wiggins, *J. Chem. Soc.*, 1815 (1938), m. p. 51–52°; $[\alpha]^{18}D$ −20.9° (*c* = 1.34, chloroform).

filtrate saturated with hydrogen sulfide. The precipitated silver sulfide was removed by filtering through a charcoal mat and the filtrate concentrated to a sirup under reduced pressure. To the residue was added 200 ml. of toluene and the solvent removed under reduced pressure. The residue was dissolved in 100 ml. of boiling isopropyl ether, and on cooling the trimethylglucose crystallized out. After twenty-four hours the crystals were filtered off and the filtrate concentrated and cooled in the refrigerator to obtain a second crop. Further concentration and cooling yielded a third crop. The total crystalline material was 8 g. (71.8%). The product was recrystallized by dissolving in 100 ml. of boiling isopropyl ether, charcoaling, and filtering the hot solution. On cooling to room temperature crystals of trimethylglucose soon formed and were filtered off. Four grams of colorless crystals (thick plates) was obtained. The compound sintered at 94° and melted at 97–98° (cor.); $[\alpha]^{25}D$ +41.1° (*c*, 1.6; *l*, 4; H_2O). The specific rotation increased to +78° at equilibrium. The data on mutarotation are given in Table I. A sample of this material was dissolved in water containing a trace of ammonia and the rotation determined, $[\alpha]^{25}D$ +77.5° (*c*, 2; H_2O).

Anal. Calcd. for $C_9H_{18}O_6$: CH_3O, 41.89. Found: 41.64.

On cooling the filtrate from the first crystallization in the refrigerator, 2.5 g. of colorless needles was obtained; m. p. 64–67° (cor.); $[\alpha]^{25}D$ +91.9° (*c*, 2; *l*, 4; H_2O). The specific rotation decreased to +77.4° at equilibrium. Data on mutarotation are given in Table I. A sample was recrystallized several times from isopropyl ether with cooling. Melting point of final product, 76–77° (cor.).

The following procedure was used in the preparation of the first sample of 3,4,6-trimethyl-D-glucose which crystallized. Five grams of methyl 3,4,6-trimethyl-β-D-glucoside was dissolved in 150 ml. of 5% aqueous hydrochloric acid and the solution refluxed for two and one-half hours. The solution was then filtered and treated with an excess of barium carbonate. A small amount of charcoal was added and the mixture filtered. The filtrate was evaporated to dryness *in vacuo* and the residue extracted with boiling chloroform. A little charcoal was added and the mixture filtered. The solvent was evaporated and the residue sirup placed in a vacuum oven overnight at 60°. The yield of thick sirup was 4 g. (84%); $[\alpha]^{25}D$ +74.2° (*c*, 1.66; H_2O).

After standing at room temperature for two months, this product was found to have partially crystallized. It was recrystallized from isopropyl ether with cooling, reserving a sample for seed crystals. The compound crystallized in the form of fine colorless needles, m. p. 77–79.5°. After another recrystallization the melting point was 78–80°. Further recrystallization produced no change in melting point.

TABLE I

MUTAROTATION OF 3,4,6-TRIMETHYL-D-GLUCOSE AT 25°°

Time in minutes	Rotation observed, °	Specific rotation, °
A. Alpha form (needles), weight of compound 0.4989 g.		
2.5	7.33	91.9
5	7.18	90.0
10	7.12	89.3
25	6.91	86.6
90	6.42	80.5
300	6.16	77.4
1050	6.16	77.4
B. Beta form (plates), weight of compound 0.4031 g.		
2.5	2.65	41.1
3.5	2.72	42.2
5	2.75	42.6
10	2.95	45.8
15	3.14	48.7
35	3.64	56.5
65	4.13	64.0
155	4.69	72.8
210	4.79	74.4
1050	5.03	78.0
1260	5.03	78.0

° Solvent, water; volume of solution, 25 ml.; length of tube, 4 dm.

Summary

3,4,6-Trimethyl-β-D-glucose and 3,4,6-trimethyl-α-D-glucose have been obtained in crystalline form.

A new synthesis of methyl 3,4,6-trimethyl-β-D-glucoside has been carried out.

IOWA CITY, IOWA RECEIVED APRIL 9, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Equilibrium in the Dehydrogenation of Secondary Propyl and Butyl Alcohols

BY HARRY J. KOLB[1] AND ROBERT L. BURWELL, JR.[1]

Introduction

Equilibrium has been studied in the dehydrogenation of but one secondary alcohol, *i*-propyl alcohol.[2] It appeared profitable to re-investigate this reaction with other techniques and to extend the study to other secondary alcohols. This paper reports the results of such investigation in the cases of *i*-propyl and *s*-butyl alcohols. The study of other secondary alcohols will be continued when circumstances permit.

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(2) Parks and Kelley, *J. Phys. Chem.*, **32**, 740 (1928).

Experimental

Materials.—Mono-*i*-propyl phthalate was twice recrystallized from ligroin and saponified. After drying with lime, the alcohol was fractionated in a 50-plate Stedman column; $d^{24.82}_4$ 0.78106.[3]

s-Butyl alcohol (Eastman Kodak Company) was fractionated in a 150-plate Podbielniak Heli-Grid column at a reflux ratio of 100 to 1 and a take-off rate of 5 ml. per hour; d^{25}_4 0.80250, $n^{25}D$ 1.3948.[4]

(3) d^{25}_4 0.78099 interpolated from the data of Timmermans and Delcourt, *J. chim. phys.*, **31**, 105 (1934). Brunel, THIS JOURNAL, **45**, 1337 (1923), gives 0.78084. Correcting our value to 25° by the temperature coefficient of Timmermans, one gets 0.78091.

(4) Brunel[3] reports d^{25}_4 0.80235; $n^{25}D$ 1.39495; Timmermans and Martin, *J. chim. phys.*, **25**, 431 (1928), report d^{25}_4 0.80299.