a solution of 1.00 g. *dl*-stilbene dichloride in 10 ml. glacial acetic acid in the same apparatus used for the conversions with silver acetate. The mixture was heated with stirring for four and one-half hours with a bath at 100–110°. The mixture was cooled and filtered, the silver chloride being washed with acetic acid. Dilution of the filtrate and washings with water yielded an oily material which soon crystallized. This was washed with water and dried over potassium hydroxide.

The dry product weighed 0.98 g. (98% recovery) and the m. p. was 86.5–91.0°; mixed m. p. with *dl*-dichloride was 89.5–92.5°. A 0.93-g. portion of this material was crystallized from hexane, yielding crops: 0.50 g., 53%, m. p. 92–94°; 0.24 g., 25%, m. p. 91–93°; 0.13 g., 13%, m. p. 89–92°; total recovery, 91%.

Summary

The diastereomeric stilbene dichlorides are transformed by silver acetate in acetic acid to the ester of a glycol predominantly *meso* when a dry solvent is used and predominantly *dl* when the solvent contains more than the stoichiometric amount of water. It seems likely that the stilbene dichlorides are first converted mainly to *erythro*-acetoxychloride. In the course of replacement of the second halogen atom, there is participation by a neighboring acetoxy group.

Los Angeles, California Received September 17, 1945

[Contribution from the Chemical Laboratory of The Ohio State University]

Sugar Interconversion under Reducing Conditions. I[1]

By M. L. Wolfrom, M. Konigsberg,[2] F. B. Moody[2] and R. Max Goepp, Jr.[3]

The reducing sugars undergo very extensive transformations when subjected to the vigorous action of strong alkali.[4] The initial or incipient reaction, demonstrable under conditions of mild alkalinity, was discovered by Lobry de Bruyn and Alberda van Ekenstein[5] and consists in the reciprocal interconversion of epimeric aldoses and their corresponding ketose. The nature of this reaction has been explained[6] by the assumption of an enediol common to the three sugars.

Lewis and co-workers[7] investigated the reciprocal interconversion of 2,3,4,6-tetramethyl-D-glucose and 2,3,4,6-tetramethyl-D-mannose in limewater (0.04 *N*) at 35°. This reaction reached a true equilibrium when the two aldoses were present in approximately equal amount. No ketose was formed since the mobile hydrogen required for ketose formation was herein replaced by a methyl group.

Fredenhagen and Bonhoeffer[8] studied the alkaline interconversion of D-glucose and tetramethyl-D-glucopyranose in a deuterium oxide solvent. The five hydroxyl groups of the former and the one hydroxyl group of the latter exchanged freely with the solvent. If an appreciable amount of enolic intermediate had been formed, a maximum of two atoms of deuterium would have been permanently fixed in the unsubstituted sugar molecule as a carbon to hydrogen bond. Similarly, a maximum of one deuterium atom would have been so bound by the methylated sugar. These predictions were borne out by experiment except that at temperatures below 40° very little bound deuterium was found in the unsubstituted sugar. The authors therefore accepted the enolic mechanism as the only satisfactory explanation of their experiments at temperatures of 40° and above but for temperatures below this, as at 25°, they proposed an entirely different mechanism involving a dimolecular intermediate. This postulated intermediate is untenable in relation to the known structure of the hexose sugars. If the enolic mechanism holds at 40° it is indeed strange that it would not likewise be valid when nothing is altered other than lowering the temperature to 25°.

In the present work we are concerned with interpreting the behavior of mildly alkaline solutions of D-glucose when placed under reducing conditions. To this end we have investigated the composition of a commercial product produced by the electro-reduction of D-glucose under conditions of mild alkalinity (*p*H 7–10) and below 30°.[9] The product was found to consist of sorbitol[10] together with small amounts of D-mannitol (*ca.* 1%) and 2-desoxysorbitol (*syn.* 2-desoxy-D-mannitol) (*ca.* 5%). The D-mannitol could arise from the reduction of D-mannose or D-fructose while the sorbitol could arise from the reduction of D-glucose or D-fructose. It is reasonable to assume that the 2-desoxysorbitol arose from the reduction to hydrocarbon of the carbonyl in the open-chain or *keto*-form of D-fructose. Numerous examples are to be found in the litera-

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[3] Research Department, Atlas Powder Company, Wilmington, Delaware.

[4] W. L. Evans, *Chem. Revs.*, **31**, 537 (1942).

[5] C. A. Lobry de Bruyn and W. Alberda van Ekenstein, *Rec. trav. chim.*, **14**, 203 (1895).

[6] A. Wohl and C. Neuberg, *Ber.*, **33**, 3099 (1900); J. U. Nef, *Ann.*, **357**, 295 (1907).

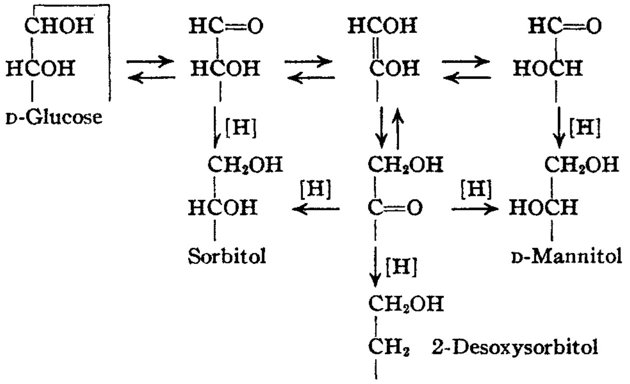
[7] M. L. Wolfrom with W. L. Lewis, This Journal, **50**, 837 (1928); R. D. Greene with W. L. Lewis, *ibid.*, 2813.

[8] H. Fredenhagen and K. F. Bonhoeffer, *Z. physik. Chem.*, **A181**, 392 (1938).

[9] H. J. Creighton, *Trans. Electrochem. Soc.*, **75**, 289 (1939); H. J. Creighton, U. S. Patents 1,612,361 (1926); 1,653,004 (1927); 1,712,951 (1929); 1,712,952 (1929); 1,990,582 (1935).

[10] We denote as sorbitol the common form of this hexitol as obtained by the reduction of D-glucose. Carbon one of this sorbitol corresponds to its precursor in D-glucose.

ture[11] of the electro-reduction of carbonyl (with aliphatic ketones and aldehydes) to hydrocarbon in acid media although not in alkaline media.[12] It would appear that the presence of the hydroxyl substituents makes the carbonyl group more susceptible to reduction in alkaline media, as it likewise makes the carbonyl compound more easily oxidizable in alkaline solution. That the open chain form of the sugar is an intermediate is supported by the fact that the cyclic sugars are reducible with hydrogen at atmospheric pressure in the presence of a platinum or palladium catalyst only in the presence of alkali.[12a] Cake[12a] has suggested that the enediol may be the intermediate reduced in the formation of hexahydric alcohols by the reduction of hexoses in alkaline media.



The isolation of small amounts of D-mannitol and of 2-desoxysorbitol from a large excess of sorbitol presents a difficult problem. A combination of crystallization and extraction methods were employed and these are diagrammed in Fig. 1. The excess of sorbitol was removed in two crops as its crystalline addition compound ($C_6H_{14}O_6 \cdot C_5H_5N$) with pyridine, a substance first described by Strain.[13] Since it was found that 2-desoxysorbitol likewise forms a crystalline addition compound ($C_6H_{14}O_5 \cdot C_5H_5N$) with pyridine, the nature of the two sorbitol–pyridine crops was investigated by conversion to crystalline sorbitol hexaacetate. A small amount of 2-desoxysorbitol (as its crystalline pentaacetate) was found in the second crop of the sorbitol–pyridine compound but none was found in the first. From the residual sirup (fraction A, Fig. 1) there was obtained a crop of crystalline D-mannitol (from ethanol). The sirup from this treatment (fraction B) was extracted with dioxane and from the extract (on solvent removal) there was obtained a crystalline crop (fraction E) of essentially pure 2-desoxysorbitol-pyridine compound. Further amounts of 2-desoxysorbitol were isolated from the mother liquor material (Fraction F) as its pentaacetate after separation from some sorbitol hexaacetate. The mother liquor material (fraction D) from fraction C was acetylated, the acetate mixture fractionated from ether–petroleum ether and so separated into three pure crystalline fractions identified as 2-desoxysorbitol pentaacetate, sorbitol hexaacetate, and D-mannitol hexaacetate.

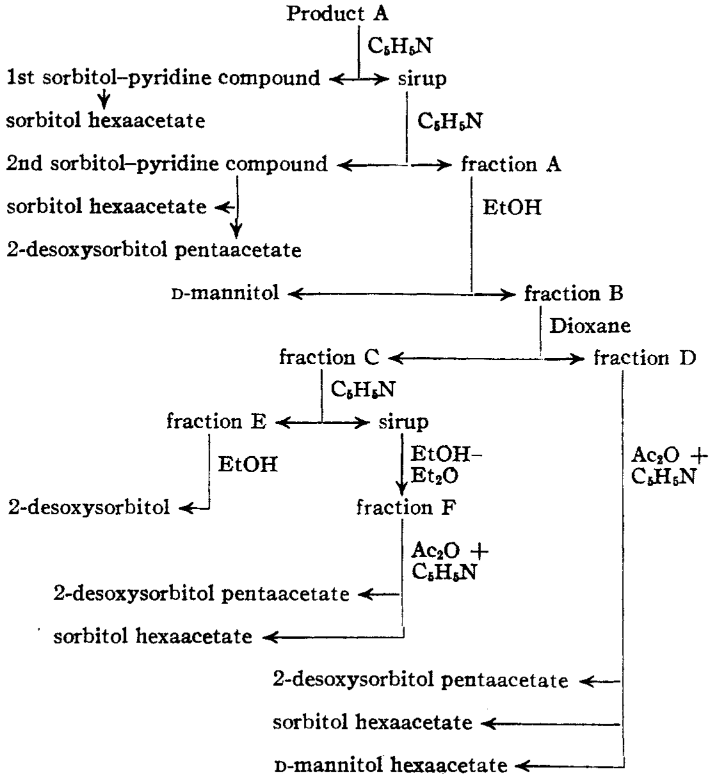


Fig. 1.—Separation flow sheet

2-Desoxysorbitol was first described by Bergmann and collaborators.[14] Its preparation (from D-glucal) was repeated in this Laboratory in order to obtain material for comparative purposes and to obtain derivatives that would be useful for its isolation and further characterization. The procedure of Bergmann and co-workers[14] was employed except that the D-glucal 3,4,6-triacetate

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[11] J. Tafel, *Ber.*, **42**, 3146 (1909); W. Schepps, *ibid.*, **46**, 2564 (1913); C. Schall and W. Kirst, *Z. Elektrochem.*, **29**, 537 (1923); E. Müller, *ibid.*, **33**, 253 (1927); S. Swann, Jr., and J. Feldman, *Trans. Electrochem. Soc.*, **67**, 195 (1935); S. Swann, Jr., and E. W. Field, *ibid.*, **72**, 327 (1937).

[12] J. Tafel and B. Emmert, *Z. Elektrochem.*, **17**, 569 (1911); C. L. Wilson and K. B. Wilson, *Trans. Electrochem. Soc.*, **80**, 151 (1941).

[12a] W. E. Cake, THIS JOURNAL, **44**, 859 (1922).

[13] H. H. Strain, *ibid.*, **56**, 1756 (1934).

[14] M. Bergmann, H. Schotte and W. Leschinsky, *Ber.*, **56**, 1052 (1923).

was saponified according to the general procedure of Helferich and Himmen[15] and the D-glucal was reduced to crystalline 2-desoxysorbitol catalytically in a high pressure bomb. That the carbon chain of 2-desoxysorbitol was normal was demonstrated by its reduction to 2-iodohexane with hydriodic acid. Since no derivatives of 2-desoxysorbitol were recorded, the following were obtained in crystalline form and characterized: pentaacetate; pentabenzoate; di-(*m*-nitrobenzylidene)-2-desoxysorbitol; pyridine addition compound (1:1). Of these, the pyridine addition compound and the pentaacetate proved to be the most useful for isolation purposes. The identity of the isolated 2-desoxysorbitol (likewise its pentaacetate and pentabenzoate) with the authentic synthetic specimens was demonstrated by melting point, mixed melting point and rotation.

Experimental

Preparation of 2-Desoxysorbitol[10] (*syn.* 2-Desoxy-D-mannitol) from 2-Desoxy-D-glucose.—An authentic sample of 2-desoxysorbitol was prepared for comparative purposes from D-glucose according to the general procedure of Bergmann and co-workers.[14] All intermediates were obtained in crystalline condition and were purified before being used in the succeeding step. The melting points of the intermediates were as follows: tetraacetyl-D-glucopyranosyl bromide, 79–80°; D-glucal triacetate, 54–55°; D-glucal, 59–60°; 2-desoxy-D-glucose, 146–148°. The method of saponification of D-glucal 3,4,6-triacetate was that of Helferich and Himmen.[15] The reduction of 2-desoxy-D-glucose was performed catalytically under pressure instead of by the sodium amalgam method employed by Bergmann and co-workers.[14]

2-Desoxy-D-glucose (10 g.) was dissolved in water (75 cc.) and mixed with several grams of kieselguhr-supported nickel catalyst. The mixture (*p*H 5.8) was placed in a shaking autoclave (American Instrument Co.) and the reduction started at 25° and a pressure of 1050 pounds. The reaction was carried out over a period of five hours, the maximum temperature being 148° and the maximum pressure 1500 pounds. The reduction mixture (*p*H 5.9) was filtered through a bed of "Super-Cel" (Johns-Manville) and the filtrate diluted with water. Hydrogen sulfide was passed into the solution until the nickel was precipitated. The precipitate was filtered and the aerated filtrate was evaporated to a thick sirup under reduced pressure. The dehydrated (with ethanol) sirup was crystallized from absolute ethanol; yield 6.5 g., m. p. 102–105°. This material was recrystallized twice from absolute ethanol, yield 5.8 g., m. p. 104–106°, $[\alpha]^{23}\text{D}$ +17.5° (23°, *c* 10, water); $[\alpha]^{28}\text{D}$ +35° (*c* 5, aqueous borax, borax *c* 10); $[\alpha]^{27}\text{D}$ +11° (*c* 3, pyridine). For 2-desoxysorbitol, Bergmann and co-workers[14] recorded the constants: m. p. 104–106°, $[\alpha]^{18}\text{D}$ +15.6° (water).

The Hydriodic Acid Reduction of 2-Desoxysorbitol.—Pure 2-desoxysorbitol (15 g.) was reduced with hydriodic acid as directed by Michael and Hartman.[16] After reduction, the iodide was converted to the acetate, this saponified to the alcohol and the 3,5-dinitrobenzoate of this alcohol was prepared according to the directions of Malone and Reid.[17] There was obtained 0.7 g. of a crystalline product, m. p. 37–38°. A mixed melting point with an authentic specimen of the 3,5-dinitrobenzoate of hexanol-2 (m. p. 37–38°) showed no depression.

2-Desoxysorbitol Pentaacetate.—Pure 2-desoxysorbitol (2 g.) was dissolved in dry pyridine (10 cc.), cooled and acetic anhydride (15 cc.) was added. The solution, after being kept at room temperature for twenty-four hours, was poured into ice and water (200 cc.). A sirup separated which soon hardened to a semi-crystalline mass. The decanted, aqueous solution was extracted with chloroform and the precipitated material was dissolved in the extract. This was washed with cold 5% sulfuric acid, water, saturated sodium bicarbonate solution and water. After drying over calcium chloride and treating with Darco decolorizing charcoal, the clear extract was evaporated to a sirup under reduced pressure. Crystallization of the product was effected from ether–petroleum ether (30–60°); yield 3.5 g., m. p. 83–85°, $[\alpha]^{24}\text{D}$ +34.5° (*c* 5, chloroform). Pure material was obtained on two more crystallizations from the same solvent mixture; m. p. 86–87°, $[\alpha]^{21}\text{D}$ +35.3° (*c* 5, chloroform).

Anal. Calcd. for $C_6H_9O_5(CH_3CO)_5$: C, 51.06; H, 6.42; CH_3CO, 13.28 cc. 0.1 *N* sodium hydroxide per 100 mg. Found: C, 51.26; H, 6.28; CH_3CO, 13.20 cc.

2-Desoxysorbitol Pentabenzoate.—Pure 2-desoxysorbitol (1 g.) was dissolved in dry pyridine (10 cc.), cooled and benzoyl chloride (6 cc.) was added. The reaction mixture, after being kept at room temperature overnight, was poured into ice and water (150 cc.). The sirup that separated was washed with cold water and dissolved in chloroform. The solution was washed with aqueous potassium bisulfate, water, saturated sodium bicarbonate solution and water. After drying over calcium chloride and treating with Darco decolorizing charcoal, the chloroform was removed. The sirup obtained was crystallized from dry ether by the addition of petroleum ether to incipient opalescence and allowing to stand at ice-box temperature for several days; yield 2.5 g., m. p. 105–107°, $[\alpha]^{23}\text{D}$ +60.5° (*c* 5, chloroform). Pure material was obtained on recrystallization in the same manner; m. p. 106–107°, $[\alpha]^{24}\text{D}$ +60.5° (*c* 5, chloroform).

Anal. Calcd. for $C_6H_9O_5(C_6H_5CO)_5$: C, 71.71; H, 4.99; C_6H_5CO, 7.28 cc. 0.1 *N* sodium hydroxide per 100 mg. Found: C, 71.55; H, 4.81; C_6H_5CO, 7.27 cc.

Di-(*m*-nitrobenzylidene)-2-desoxysorbitol.—This derivative was prepared according to the general directions of Bleyer, Diemair and Lix.[18] Pure 2-desoxysorbitol (2 g.) was dissolved in concentrated hydrochloric acid (5 cc.) and *m*-nitrobenzaldehyde (5 g.), dissolved in butyl acetate (25 cc.), was added. The mixture was shaken from time to time and kept in the ice-box for several days. Water (50 cc.) was added and the butyl acetate evaporated. The sirup that separated was dissolved in ethyl acetate, cooled, petroleum ether added to opalescence, and placed at ice-box temperature for several hours. The crystalline product was removed by filtration; yield 1.6 g., m. p. 165–170°. This product was recrystallized three times in the same manner; m. p. 176–177°, $[\alpha]^{28}\text{D}$ +12.5° (*c* 2, ethyl acetate); $[\alpha]^{30}\text{D}$ −10° (*c* 2, pyridine).

Anal. Calcd. for $C_{20}H_{20}O_9N_2$: C, 55.55; H, 4.66; N, 6.48. Found: C, 55.55; H, 4.95; N, 6.02.

2-Desoxysorbitol–pyridine (1:1) Addition Compound.—Pure 2-desoxysorbitol (2 g.) was dissolved in hot pyridine (10 cc.) and cooled in the ice-box for twenty-four hours. The crystalline compound was filtered, washed with cold pyridine, and thoroughly with anhydrous ether; yield 2.7 g., m. p. 73–75°. A second crop (0.2 g.) was obtained from the filtrate, giving a total return of 98% based on a 1:1 pyridine addition compound.

Anal. Calcd. for $C_6H_{14}O_5 \cdot C_5H_5N$: C_5H_5N, 32.25. Found: C_5H_5N, 32.16 (loss in weight at 25°, 25 mm., 60 hours).

Material Subjected to Analysis.—The material (denoted as product A) subjected to the analytical investigation herein described was received from the Atlas Powder Company of Wilmington, Delaware. It was a comparatively sorbitol[10]-rich product manufactured by the electroreduction of D-glucose under conditions of relatively low alkalinities (*p*H 7–10), and below 30°, according to the

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(15) B. Helferich and E. Himmen, *Ber.*, **61**, 1835 (1928).

(16) A. Michael and R. N. Hartman, *ibid.*, **40**, 142 (1907).

(17) G. B. Malone and E. E. Reid. This Journal, **51**, 3424 (1929).

(18) B. Bleyer, W. Diemair and G. Lix, *Z. Untersuch. Lebensm.*, **65**, 37 (1933).

general operating conditions described in United States Patent 1,990,582.[9] The product was a thick sirup of a light straw color; $n^{20}\mathrm{D}$ 1.4824, d^{20}_{4} 1.341, $[\alpha]^{27}\mathrm{D}$ +0.4° (*c*, 20.8, water).

Anal. Moisture, 21.8; ash, 0.57; reducing sugar as D-glucose, 0.05; SO_4 as Na_2SO_4, 0.49.

Removal of Excess Sorbitol.—The initial material (1 kg.) was dissolved in warm ethanol (95%, 1.5 liters) and concentrated to a thick sirup under reduced pressure. Solution and concentration were repeated and the alcohol completely removed. This dried sirup was dissolved in pyridine (2.5 kg.) and crystallization of the sorbitol-pyridine (1:1) addition compound was initiated by seeding after cooling to room temperature. The crystalline material was filtered after standing at room temperature for twenty-four hours and at ice-box temperature for an additional twenty-four hours; yield *ca.* 1 kg. of air-dried sorbitol–pyridine compound. A 25-g. portion of this air-dried material attained a constant weight of 18.8 g. when dried at room temperature over concentrated sulfuric acid at reduced pressure. According to Strain,[13] such a procedure will not decompose the sorbitol–pyridine compound. The weight of sorbitol–pyridine compound freed of excess pyridine was thus 752 g. Acetylation (pyridine–acetic anhydride) of a 10-g. portion of the vacuum-dried complex followed by exhaustive fractional crystallization of the acetate from acetone–petroleum ether yielded 16.05 g. of pure sorbitol hexaacetate (m. p. 98–100°) or 97% of the theoretical yield from pure sorbitol–pyridine (1:1). No 2-desoxysorbitol pentaacetate was found.

The filtrate from the above sorbitol–pyridine compound was concentrated to a sirup, dehydrated with ethanol (95%) and again crystallized from pyridine, yielding approximately 100 g. of air-dried crystalline material. This yielded 79.2 g. of product when freed of excess pyridine by drying at room temperature over concentrated sulfuric acid under reduced pressure. Acetylation (pyridine-acetic anhydride) of a 10-g. portion of this material followed by exhaustive fractional crystallization from acetone–petroleum ether yielded 15.3 g. (92%) of pure sorbitol hexaacetate (m. p. 98–100°) and 0.1 g. (0.6%) of 2-desoxysorbitol pentaacetate. This amount of 2-desoxysorbitol pentaacetate represents 0.04% (dry basis) of the amount of initial sirup employed.

All of the above operations were carried out in a laboratory well-nucleated with 2-desoxysorbitol-pyridine (1:1) compound. It is therefore demonstrated that sorbitol, essentially uncontaminated with 2-desoxysorbitol, can be removed by the procedure described.

Complete pyridine removal from the filtrate obtained from the second sorbitol–pyridine compound was effected by dilution with water and removal of the solvent under diminished pressure. This was repeated until no odor of pyridine was detected and the sirup was then dehydrated with ethanol as described above; yield 120 g. of dried sirup (fraction A, Fig. 1).

Isolation of D-Mannitol.—Fraction A was dissolved in absolute ethanol (2 liters), cooled, seeded with D-mannitol and held at ice-box temperature for several days. The crystalline product was removed by filtration (15 g.) and recrystallized four times from 95% ethanol; yield 6.1 g., m. p. 164–166°, $[\alpha]^{20}\mathrm{D}$ −0.3° (*c* 3.4, water), $[\alpha]^{20}\mathrm{D}$ +29.6° (*c* 4.5, aqueous borax, borax *c* 9). A mixed melting point with an authentic sample of D-mannitol (m. p. 166–167°) was unchanged.

A portion of this material was acetylated and the product obtained was recrystallized from aqueous alcohol. The acetate had these constants: m. p. 123–125°; $[\alpha]^{20}\mathrm{D}$ +25° (*c* 5, chloroform). A mixed melting point with an authentic sample of D-mannitol hexaacetate (m. p. 124–125°; $[\alpha]^{20}\mathrm{D}$ +25°, chloroform) was unchanged.

Fraction C.—The residual sirup (fraction B, 112 g.) obtained was extracted with hot dioxane (2 liters) in the following manner: the sirup was placed in a 3-liter round-bottomed flask fitted with a mechanical stirrer and after addition of the dioxane, the mixture was heated to 80–90° on a water-bath. The mixture was vigorously agitated for one to two hours and cooled to room temperature. The clear supernatant liquid was decanted from the separated sirup and placed at ice-box temperature. The crystalline product was filtered, washed with anhydrous ether, and dried. A total of five such extractions were made and 57.5 g. of crude product was obtained. The melting point of the material obtained from the several extractions varied between 72–86° and the specific rotation in water varied from +12 to +16°. All of this dioxane-extracted material was combined and is designated fraction C.

Fraction E.—Fraction C (57 g.) was dissolved in hot pyridine (300 cc.), cooled in an ice-bath and the whole placed in the ice-box overnight. The crystalline material was removed by filtration, washed with cold pyridine, thoroughly washed with dry ether, and quickly air-dried; yield 45 g. of crude product (fraction E); m. p. 70–75°, $[\alpha]^{23}\mathrm{D}$ +7.2° (*c* 5, pyridine). This material lost 31% of its weight when dried in a vacuum desiccator (25 mm.) over sulfuric acid for sixty hours; calcd. for a monopyridine-desoxyhexitol compound, $C_6H_{14}O_5 \cdot C_5H_5N$: 32.25%.

Isolation of 2-Desoxysorbitol.—The pyridine-free, crystalline product obtained from fraction E (31 g.) had the following constants: m. p. 83–87°, $[\alpha]^{24}\mathrm{D}$ +16° (*c* 5, water). This material was recrystallized from absolute ethanol (15 parts); m. p. 102–105°, $[\alpha]^{24}\mathrm{D}$ +16.7° (*c* 3, water). Pure material was obtained on two more crystallizations from absolute ethanol; total yield of pure product 28 g., m. p. 104–106° unchanged on admixture with an authentic specimen of 2-desoxysorbitol, $[\alpha]^{24}\mathrm{D}$ +17.5° (*c* 10, water), $[\alpha]^{24}\mathrm{D}$ +35° (*c* 5, aqueous borax, borax *c* 10), $[\alpha]^{27}\mathrm{D}$ +10.7° (*c* 3, pyridine). The pentabenzoate was prepared according to the procedure described above; m. p. 106–107° unchanged on admixture with an authentic specimen of 2-desoxysorbitol pentabenzoate, $[\alpha]^{24}\mathrm{D}$ +60.5° (*c* 5, chloroform). These constants are in agreement with those described above for 2-desoxysorbitol and its pentabenzoate.

Anal. Calcd. for $C_6H_{14}O_5$: C, 43.37; H, 8.49. Found: C, 43.22; H, 8.40.

It thus is evident that fraction C was impure 2-desoxysorbitol and that fraction E was the nearly pure monopyridine addition compound of 2-desoxysorbitol.

Fraction F.—The pyridine mother liquors, resulting from the crystallization of fraction E, were completely freed of pyridine and the dehydrated sirup was dissolved in absolute ethanol. The addition of dry ether to incipient opalescence and cooling for several days, resulted in the crystallization of a product; yield 9 g., m. p. 65–75°. A second crop was obtained from the filtrate; yield 2.3 g., m. p. 72–75°. The purification of this material (fraction F) was rather difficult. It was recrystallized several times from ethanol by the addition of ether and allowing the solution to slowly evaporate at room temperature. The constants, of the material purified in this manner, were: m. p. 81–83°, $[\alpha]^{23}\mathrm{D}$ +10° (*c* 5, water). A combustion analysis indicated that this product could have been a mixture of any two of the following compounds: hexitol, $C_6H_{14}O_6$; desoxyhexitol, $C_6H_{14}O_5$; anhydrohexitol, $C_6H_{12}O_5$.

A portion of purified fraction F (5 g.) was acetylated as described above and the product was fractionated from ether–petroleum ether (30–60°). This purification produced: 3.0 g., m. p. 99–100°, $[\alpha]^{30}\mathrm{D}$ +9.6° (*c* 4.4, chloroform), mixed melting point with sorbitol hexaacetate (m. p. 99–100°) unchanged; 4.8 g., m. p. 85–87°, $[\alpha]^{29}\mathrm{D}$ +34.8° (*c* 5, chloroform), mixed melting point with 2-desoxysorbitol (m. p. 86–87°) unchanged. This indicated that fraction F was a mixture of sorbitol and 2-desoxysorbitol.

A 1:1 mixture of sorbitol and 2-desoxysorbitol did not crystallize from ethanol–ether solution. A 1:2 mixture of sorbitol and 2-desoxysorbitol crystallized from alcohol–ether solution to produce a substance, m. p. 81–83°, $[\alpha]^{28}\mathrm{D}$ +10° (*c* 5, water), which apparently was identical with purified fraction F. A 1:3 mixture of sorbitol and 2-desoxysorbitol gave a product, m. p. 80–83°, $[\alpha]^{30}\mathrm{D}$ +11° (*c* 5, water), which did not depress the melting point of purified fraction F.

The Identification of Sorbitol, 2-Desoxysorbitol and D-Mannitol in the Residual Sirup, Fraction D.—Fraction D was dehydrated by ethanol distillation under reduced pressure and a portion of this (7 g.) was acetylated with acetic anhydride and pyridine. The product obtained was fractionated from ether–petroleum ether (30–60°) and produced three fractions of crystalline material: (1) 4.5 g., m. p. 98–100°, $[\alpha]^{25}D$ +9.8° (*c* 5, chloroform), mixed melting point with a pure specimen of sorbitol hexaacetate (m. p. 99–100°) unchanged; (2) 2.3 g., m. p. 85–87°, $[\alpha]^{25}D$ +34.5° (*c* 5, chloroform), mixed melting point with a pure specimen of 2-desoxysorbitol pentaacetate (m. p. 86–87°) unchanged; (3) 0.2 g., m. p. 122–124°, $[\alpha]^{25}D$ +23.6° (*c* 5, chloroform), mixed melting point with a pure specimen of D-mannitol hexaacetate (m. p. 124–125°) unchanged.

Summary

1. Crystalline 2-desoxysorbitol has been obtained in approximately 5% yield from a commercial sorbitol-rich product manufactured by the electro-reduction of D-glucose at *p*H 7–10.

2. Crystalline D-mannitol has been isolated in approximately 1% yield from the same source.

3. The results of 1 and 2 are in harmony with an enolic mechanism of sugar interconversion under reducing conditions.

4. 2-Desoxysorbitol forms a monopyridine addition compound which, in the pure state, is quite insoluble in pyridine.

5. The crystalline pentaacetate, pentabenzoate, and di-*m*-nitrobenzylidene derivatives of 2-desoxysorbitol have been synthesized and characterized.

COLUMBUS, OHIO RECEIVED OCTOBER 17, 1945

[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

The Synthesis of Δ¹-Pyrrolines[1]

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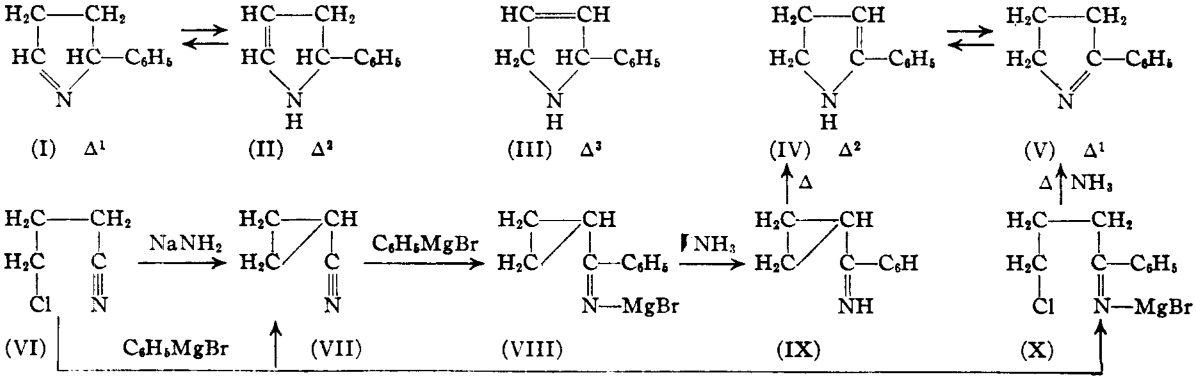
Pyrroline Structure.—Five partial reduction products of 2-phenylpyrrole may be formulated as shown in structures (I)–(V). 2-Phenyl-Δ³-pyrroline (III), whose structure involves no special problems, was described by Wohl.[3] 2-Phenyl-Δ²-pyrroline (IV) was reported by Gabriel and Coleman,[4] and recently 5-phenyl-Δ²-pyrroline (II) was announced by Gitsels and Wibaut.[5] Most workers on pyrrolines, *e. g.*, Mascarelli and Testoni,[6] have been reluctant to formulate such pyrrolines as those of Gabriel and Coleman and of Gitsels and Wibaut as the Δ¹ form, namely, (V) and (I), respectively. In this connection, Taylor and Baker[7] write, "Δ¹-Pyrrolines are unknown as individuals; they are possibly tautomeric with the Δ²-pyrrolines." This tautomerism in the case of 2-phenylpyrroline (IV ⇆ V) was also suggested by one of us[8] in view of the fact that one of our syntheses suggested the Δ¹ and another the Δ² structure.



In our first synthesis of 2-phenylpyrroline, phenylmagnesium bromide was allowed to react with γ-chlorobutyronitrile (VI). Although this reaction may proceed along several paths,[9] the main product is the N-bromomagnesium derivative of phenyl γ-chloropropyl ketimine (X), which will give the pyrroline by ammonolysis,[8] careful hydrolysis[8] or pyrolysis, *e. g.*, in xylene.[10] If we ignore the possible tautomerism of the intermediates, the foregoing synthesis indicates the Δ¹ structure (V). In our second synthesis, the 2-phenylpyrroline was obtained by the pyrolytic rearrangement of phenyl cyclopropyl ketimine (IX), which was obtained from (VI) *via* (VII) and

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[3] Wohl, *Ber.*, **34**, 1922 (1901).

[4] Gabriel and Colman, *ibid.*, **41**, 513 (1908).

[5] Gitsels and Wibaut, *Rec. trav. chim.*, **60**, 50 (1941).

[6] Mascarelli and Testoni, *Gazz. chim. ital.*, **33**, 312 (1903).

[7] Taylor and Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, 1937, p. 491.

[8] Cloke, THIS JOURNAL, **51**, 1174 (1929).

[9] Cloke, Baer, Robbins and Smith, *ibid.*, **67**, 2155 (1945).

[10] Craig, Bulbrook and Hixon, *ibid.*, **53**, 1831 (1931).