[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Sugar Interconversion under Reducing Conditions. III[1,2]

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In a preceding communication,[1] the following components were reported as present in a commercial product, designated product B, manufactured by the electroreduction of D-glucose at *p*H 10–13: sorbitol,[5] 2-desoxysorbitol, D-mannitol, and 1-desoxy-D-mannitol. It was shown that the formation of these substances was easily explained by a mechanism of 1,2-enolization followed by the electroreduction of the carbonyl group to the hydrocarbon stage. In addition, the formation of 1-desoxysorbitol as a component of the mixture was predicted. In the present work 1-desoxysorbitol and several useful derivatives of it were synthesized and employed for nucleation but it was not found in any of the fractions studied. 1-Desoxy-D-mannitol was likewise not encountered in the present work. Our results (the preponderance of 2-desoxyhexitols over 1-desoxyhexitols) verify the known fact that ketoses are more readily reducible than aldoses.[6] The hexitols isolated likewise may have arisen mainly from the ketoses rather than the aldoses. Cantor and Peniston[7] have shown that the ease of reduction of a number of aldohexoses at the dropping mercury cathode was in the following decreasing order: L-allose, D-galactose, D-mannose and D-glucose. The fact that D-glucose occupies the lowest position would also augur for the presence of smaller quantities of 1-desoxysorbitol in the product under immediate investigation. Caution is, however, required in accepting conclusions based upon the isolation or non-isolation of products from such a complex and difficultly separable mixture as product B.

1-Desoxysorbitol (*syn.* L-gulomethylitol) has been described by Müller and Reichstein[8] and its pentaacetate by Gätzi and Reichstein.[9] In the present work 1-desoxysorbitol pentaacetate was synthesized by the high-pressure catalytic reduction of 1-desoxy-*keto*-D-fructose tetraacetate[10] with subsequent acetylation. Fortunately, only the known sorbitol derivative crystallized from the reaction mixture. 1-Desoxysorbitol was obtained on saponification of its pentaacetate and from this a crystalline dimethylene-1-desoxysorbitol was obtained on formalation and this derivative was further characterized by the synthesis of its crystalline monoacetate.

In the present work the following new components of product B have been established: allitol, a 2-desoxyhexitol of undetermined configuration, and (in small amounts) a pentitol of unknown structure. The latter, a fragmentation product, arises from the vigorous action of alkali under reducing conditions. Fragmentation and saccharinic acid formation occur under strongly alkaline conditions but the reactions leading to them proceed to some extent under milder conditions. Thus, Goepp and Soltzberg[11] determined the types of carbon nuclei present in a similar but not identical product and established the presence, in relatively minor quantities, of five-carbon compounds. Among these was one having the carbon skeleton of 2-methylbutane, derived from a branched chain desoxypentitol.

The pentitol found in the present work was obtained in the form of its crystalline dimethylene and dimethylene monoacetate derivatives. These were optically active, a fact which eliminates xylitol and adonitol (*syn.* ribitol) from consideration, for although an optically active (by substitution) dimethylene-L-xylitol[12] is known, such types of optically active derivatives would not be encountered in our work since we formalated the parent meso-alcohol. Dimethylene-arabitol was then synthesized as a sirup which failed to crystallize on nucleation with our crystalline material.[13] It is thus probable that the parent pentitol of our isolated derivative has a branched-chain structure in harmony with the work of Goepp and Soltzberg.[11]

The isolation of allitol indicates that the 2,3-enediolic structure was present in the alkaline sugar mixture undergoing electroreduction. Lobry de Bruyn and Alberda van Ekenstein[14] demonstrated that in the alkaline conversion of D-glucose to D-fructose, the latter was accompanied by another ketose designated by them pseudo-fruc-

(1) Preceding communication in this series: M. L. Wolfrom, F. B. Moody, M. Konigsberg and R. M. Goepp, Jr., THIS JOURNAL, **68**, 578 (1946).

(2) Presented in part before the Division of Sugar Chemistry and Technology at the 107th Meeting of the American Chemical Society, Cleveland, Ohio, April 6, 1944.

(3) Atlas Powder Company Research Associate of The Ohio State University Research Foundation, 1941–1945.

(4) Research Department, Atlas Powder Company, Wilmington Delaware.

(5) 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.

(6) J. Heyrovský and I. Smoler, *Coll. Czechoslov. Chem. Commun.*, **4**, 521 (1932).

(7) S. M. Cantor and Q. P. Peniston, THIS JOURNAL, **62**, 2113 (1940).

(8) H. Müller and T. Reichstein, *Helv. Chim. Acta*, **21**, 259 (1938).

(9) K. Gätzi and T. Reichstein, *ibid.*, **21**, 921 (1938).

(10) M. L. Wolfrom and R. L. Brown, THIS JOURNAL, **65**, 1521 (1943).

(11) R. M. Goepp, Jr., and S. Soltzberg, paper presented before the Division of Sugar Chemistry and Technology at the 99th Meeting of the American Chemical Society, Cincinnati, Ohio, April 11, 1940; *cf.* K. R. Brown, U. S. Patent 2,172,357 (1940).

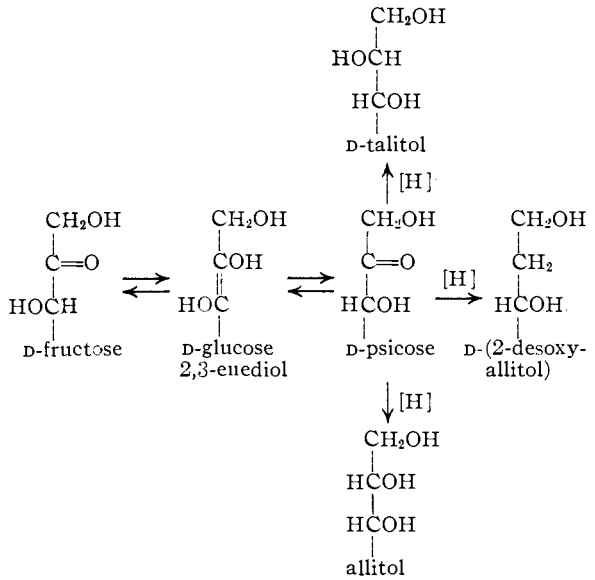
(12) A. T. Ness, R. M. Hann and C. S. Hudson, THIS JOURNAL, **66**, 665 (1944).

(13) This fact was verified on a similar sample by Dr. R. M. Hann of the Chemistry Laboratory, U. S. National Institute of Health, Bethesda, Maryland.

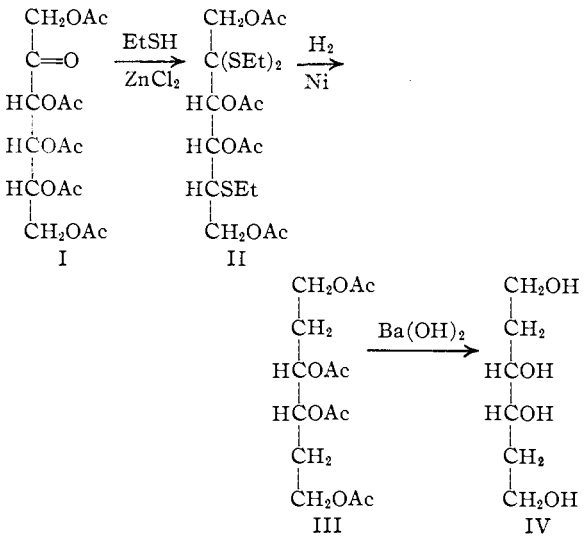
(14) C. A. Lobry de Bruyn and W. Alberda van Ekenstein, *Rec. trav. chim.*, **16**, 257, 274 (1897).

tose. Nef[15] postulated that this ketose should have the configuration of the ketose of the D-allose, D-altrose series. Many years later Steiger and Reichstein[16] prepared (in amorphous form) and characterized this ketose and Zerban and Sattler[17,18] proved that it was the pseudo-fructose of Lobry de Bruyn and Alberda van Ekenstein. For reasons already stated,[16b] we prefer the name D-psicose (rather than D-pseudo-fructose or D-allulose).

In addition to the products obtainable from the 1,2-enediol mechanism previously presented,[1] the following predictable components arise from the 2,3-enediol. These are allitol, D-talitol and D-(2-desoxyallitol). The last-named substance is at



present unknown. A 2-desoxyhexitol was isolated in the present work. Although the presumption is that this substance is D-(2-desoxyallitol), adequate proof has not been furnished. One route to this substance by a synthetic method establishing its structure and configuration would be by the carbonyl reduction of *keto*-D-psicose pentaacetate according to the procedure of Wolfrom and Karabinos,[19] who effected an analogous conversion of *keto*-D-fructose pentaacetate to 2-desoxysorbitol pentaacetate. The steps concerned are the conversion of the *keto*-acetate to the acetylated thioacetal according to the method of Wolfrom and Thompson[20] followed by the hydrogenolysis of the acetylated thioacetal. Final deacetylation should then yield the 2-desoxyhexitol having the configuration of the initial ketose. Although crystalline *keto*-D-psicose pentaacetate (I) was available,[16b] application of these reactions led only to sirupy products except in the last step wherein the final reduced structure was isolated in crystalline form and characterized as its crystalline dimethylene derivative. The alcohol was not, however, the expected D-(2-desoxyallitol) but was a didesoxyhexitol. Since it was optically inactive throughout the visible spectrum, it can only have the structure 1,6-(*erythro*-3,4)-hexanetetrol (IV). During the initial mercaptalation of keto-D-psicose pentaacetate (I) an acetate group on carbon 5 had been replaced by the thioethoxyl group. An intermediate hydrolysis of this acetate group before replacement may have been involved. Such an acetate replacement is not unknown.[21] Probably the desired product was also present in the reaction mixtures but failed to be crystallized. The sequence of reactions concerned is shown below.



In the present work, the very rare hexitol allitol was isolated in crystalline condition and was further characterized by one known derivative (the hexaacetate) and four new crystalline derivatives, namely, monomethylene-allitol, dimethylene-allitol, and the diacetate and dilaurate of the latter. In a comprehensive study of the relation between configuration and structure in the methylene acetals of polyhydroxy alcohols, Hann and Hudson[22] have predicted that the preferred orientation for dimethylene-allitol would be 2,4:3,5. A periodate analysis on the monomethylene-allitol showed a consumption of one mole of oxidant with the production of one mole of formaldehyde and no formic acid, a result given uniquely by the 2,4-derivative. Therefore monomethylene-allitol is established as D,L-(2,4-monomethylene-allitol). Dimethylene-allitol consumed no periodate. Since the monomethylene-allitol was obtained from it, the placement of one of the methylene groups as 2,4 is certain. The di-*p*-toluenesulfonate of the

(15) J. U. Nef, *Ann.*, **403**, 208, 362 (1914).

(16) (a) Marguerite Steiger and T. Reichstein, *Helv. Chim. Acta*, **19**, 184 (1936); *cf.* (b) M. L. Wolfrom, A. Thompson and E. F. Evans, THIS JOURNAL, **67**, 1793 (1945).

(17) F. W. Zerban and L. Sattler, *ibid.*, **64**, 1740 (1942).

(18) Zerban and Sattler, *Ind. Eng. Chem.*, **34**, 1180 (1942).

(19) M. L. Wolfrom and J. V. Karabinos, *ibid.*, **66**, 909 (1944).

(20) M. L. Wolfrom and A. Thompson, *ibid.*, **56**, 880 (1934).

(21) M. L. Wolfrom and A. Thompson, *ibid.*, **56**, 1804 (1934).

(22) R. M. Hann and C. S. Hudson, *ibid.*, **66**, 1909 (1944).

dimethylene-allitol was synthesized and both of the *p*-toluenesulfonate groups therein were found to be replaceable by iodine with sodium iodide (as determined by the amount of sodium *p*-toluenesulfonate isolated from the reaction). Such replaceability by iodine is characteristic of *p*-toluenesulfonate groups attached to primary alcohol groups. Therefore positions one and six in the dimethylene-allitol are unsubstituted, thus leaving only positions three and five for the second methylene group. The structure of dimethylene-allitol is thus 2,4:3,5 and the prediction of Hann and Hudson[22] is verified.

The identity of the allitol isolated was also established by comparison with a synthetic specimen of 2,4:3,5-dimethylene-allitol (and its diacetate). To this end, allitol was synthesized by the high pressure catalytic reduction of *keto*-D-psicose pentaacetate[16b] and the product was successively deacetylated and formalated. From the reaction mixture the allitol separated as its crystalline 2,4:3,5-dimethylene derivative uncontaminated with the methylene derivative of the diastereoisomeric D-talitol. Identification of the allitol fraction was certain because of its optical inactivity throughout the visible spectrum. The constants of the allitol (and its hexaacetate) are also in agreement with those cited by Lespieau and Wiemann,[23] who first synthesized this hexitol by hydroxylation of divinylglycol, and by Steiger and Reichstein,[16a] who established its structure unequivocally by synthesis from D-allose.

The method of isolation used in the present work consisted of a combination of crystallization and extraction procedures as outlined in Fig. 1. The excess sorbitol was removed as the pyridine (1:1) compound and some D-mannitol was then removed by crystallization from ethanol. The residual sirup was then formalated and there was isolated by crystallization techniques the methylene derivatives of sorbitol, D-mannitol, allitol and the 2-desoxyhexitol of undetermined configuration. The mother liquor material was then lauroylated and 2,4:3,5-dimethylene-allitol di-

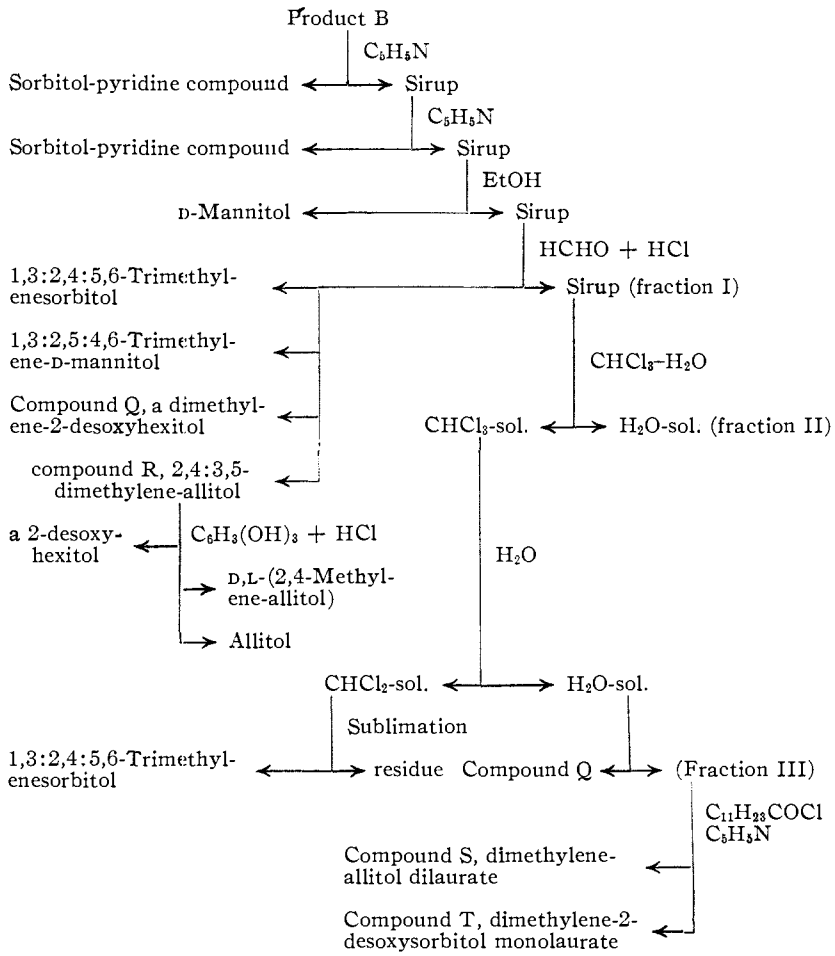


Fig. 1.—Separation flow sheet.

laurate and dimethylene-2-desoxysorbitol monolaurate were isolated in crystalline condition. It was thought that the large laurate radical might make a better differentiating group for these substances. This was not borne out by the experiments and the laurate group was not found as advantageous as the more readily attached and manipulated acetate group. The dimethylenepentitol is not shown on the flow sheet of Fig. 1 because it was isolated from a dioxane-extracted sirup.

In the course of the above work there was devised a formalation procedure that gave complete formalation of sorbitol and D-mannitol in practically quantitative yields. A deformalation procedure was also needed and one was devised which was an adaptation of the procedure of Späth and Quietensky.[24]

Experimental[25,26]

Fomalation of Sorbitol.[5]—An amount of 25 g. of sorbitol was dissolved in 75 cc. of warm, 40% aqueous formalde-

(23) R. Lespieau and J. Wiemann, *Compt. rend.*, **195**, 886 (1932); *Bull. soc. chim.*, [4] **53**, 1107 (1933); J. Wiemann, *Ann. chim.* [11] **5**, 316 (1936).

(24) E. Späth and H. Quietensky, *Ber.*, **60**, 1882 (1927).

(25) Unless otherwise noted, chloroform rotations were taken in U. S. P. (United States Pharmacopoeia) chloroform and in tubes (sometimes semimicro) of 2 dm. length.

(26) All experimentally determined melting points are corrected unless otherwise noted.

hyde, the solution cooled to 0° and 70 g. of dry hydrogen chloride gas passed in while maintaining the temperature at 0°. The solution was then heated slowly to 85° and maintained at that temperature for ninety minutes. The solution was then concentrated under reduced pressure to three-fourths volume and maintained overnight at icebox temperature; yield 21 g. of trimethylenesorbitol, m. p. 213–217°. Ness, Hann and Hudson[12] recorded the m. p. 212–216° for 1,3:2,4:5,6-trimethylenesorbitol. More material was obtained from the chloroform extract of the residue obtained on concentration to dryness (reduced pressure) of the mother liquor; yield 6 g. (total yield 91%) of slightly lower purity.

Isolation of Compounds Q and R; Formalation Procedure A.—An amount of 250 g. of sirup (from product B) from which the excess sorbitol and D-mannitol had been removed as previously described,[1] was formalated as described above with some modification (formalation procedure A). The reaction mixture was heated slowly to 85° over a period of three hours and during the heating 200 cc. of 40% aqueous formaldehyde solution was dropped in slowly. The cooled solution was diluted with 1 liter of water and neutralized with an excess of lead carbonate. The filtrate from the lead salts was treated with just sufficient hydrogen sulfide to remove the lead ion (an excess of hydrogen sulfide caused the separation of the insoluble reaction product of hydrogen sulfide and formaldehyde), filtered, and the filtrate treated with an excess of silver carbonate and again filtered. The filtrate was concentrated under reduced pressure to a volume of about 2 liters. An amount of 10.4 g. of a mixture consisting essentially of 1,3:2,4:5,6-trimethylenesorbitol and 1,3:2,5:4,6-trimethylene-D-mannitol separated and was removed by filtration at this point. Fractional crystallization from 95% ethanol gave 1,3:2,4:5,6-trimethylenesorbitol, m. p. 214–216°, mixed m. p. with authentic sample unchanged; and 1,3:2,5:4,6-trimethylene-D-mannitol, m. p. 228–229°,[27] mixed m. p. with authentic sample unchanged. On further concentration of the filtrate from the 10.4 g. crop to about one liter, a second crop of crystals separated, and was removed by filtration; yield 20 g. For purposes of future reference the filtrate will be designated fraction I (*cf.* Fig. 1).

From the above 20-g. lot of crystals there were separated three essentially pure fractions of crystals by a laborious process involving separations based upon differing solubilities in chloroform, ethanol and water. These fractions were: 1,3:2,5:4,6-trimethylene-D-mannitol,[27] 70 mg., identification by m. p. and mixed m. p.; compound Q, 1.0 g., m. p. 196–197°; compound R, 1.3 g., m. p. 250–251°.

Further quantities of compound Q, together with some 1,3:2,4:5,6-trimethylenesorbitol, were isolated from fraction I. The above filtrate (fraction I) was concentrated under reduced pressure to a volume of 400 cc. and extracted five times with chloroform (total volume, 1 liter). This chloroform-extracted aqueous solution, designated fraction II (*cf.* Fig. 1), is under further investigation. The combined chloroform extracts were concentrated under reduced pressure to a volume of 400 cc. and extracted with water six times. The water extract obtained from the first four extractions (with a total of 500 cc. of water) was kept apart from the fifth and sixth extractions (of 100 cc. each). The extract of 500 cc. will be designated fraction III. From the 200 cc. obtained on the fifth and sixth extraction, after concentration and recrystallization from absolute ethanol, there was obtained a further quantity of compound Q; m. p. 202–203°. From the final residual chloroform solution there was isolated, after sublimation and crystallization from water, a further quantity of 1,3:2,4:5,6-trimethylenesorbitol (identification by m. p. and mixed m. p.).

Identification of Compound Q as a Dimethylene-2-desoxyhexitol; Characterization of Its Monoacetate;[28] **Isolation of the Parent 2-Desoyhexitol of Undetermined Configuration; Deformalation Procedure B.**—Pure compound Q possessed the following constants on crystallization from absolute ethanol: m. p. 202–203°, $[\alpha]^{29}D$ +20° (*c* 1.2, pyridine).

Anal. Calcd. for $C_8H_{13}O_4(OH)$: C, 50.57; H, 7.43; hydroxyl value,[29] 5.26 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 190.2. Found: C, 50.25; H, 7.32; hydroxyl value, 5.34 cc.; mol. wt. (Rast), 198.

On acetylation with pyridine and acetic anhydride a monoacetate was obtained; m. p. 166–167° on crystallization from 95% ethanol, $[\alpha]^{24}D$ +20° (*c* 1.2, $CHCl_3$).

Anal. Calcd. for $C_8H_{13}O_5(COCH_3)$: C, 51.72; H, 6.95; CH_3CO, 4.3 cc. 0.1 *N* NaOH per 100 mg. Found: C, 51.70; H, 6.95; CH_3CO, 4.6 cc.

Compound Q was deformalated to the parent substance. The method employed (deformalation procedure B) was established in this Laboratory by Dr. F. B. Moody who prepared sorbitol and D-mannitol (as their hexaacetates) in *ca.* 70% yield from their trimethylene derivatives.

An amount of 500 mg. of compound Q was refluxed for four hours with 20 cc. of 5% aqueous hydrochloric acid containing 1.2 g. of phloroglucinol dihydrate. After standing overnight at room temperature the red precipitate of the condensation product between formaldehyde and phloroglucinol[30] was filtered and washed with water; 11.8% CH_2 (calcd., 14.75). The filtrate was extracted thrice with equal volumes of ether and the aqueous solution was neutralized with silver carbonate, filtered (decolorizing carbon) and concentrated to dryness under reduced pressure. The sirup (0.3 g.) so obtained crystallized in colorless needle-like crystals which were purified from ethanol–petroleum ether–ether; m. p. 74–76°, amount of pure material insufficient for polarization.

Anal. Calcd. for $C_6H_{14}O_5$: C, 43.37; H, 8.49. Found (on a slightly impure sample): C, 43.83; H, 8.82. Calcd. for a 1-desoxyhexitol on periodate oxidation (as moles per mole substance): oxidant consumed, 3; acidity, 2; formaldehyde, 1. Found: 2.8, 1.7 and 0.9, respectively.

Synthesis of 1,6-(*erythro*-3,4)-Hexanetetrol.—Crystalline *keto*-D-psicose pentaacetate[15b] (2.0 g.) was treated with ethyl mercaptan and zinc chloride as described for the synthesis of pentaacetyl-D-fructose diethyl thioacetal[20] and the product was isolated in the same manner; yield 2.2 g. (sirup). The sirupy product was subjected to hydrogenolysis as described by Wolfrom and Karabinos[19]; yield 0.9 g. (sirup, non-reducing toward Fehling solution). This sirup was saponified with barium hydrate and after removal of barium ion as carbonate and sulfate, the solution yielded a partially crystalline product (0.5 g.) on solvent removal. Pure material in the form of elongated prisms (very soluble in water and ethanol) was obtained on recrystallization from ethanol–petroleum ether; m. p. 121–122°, $[\alpha]^{25}$ 0° (throughout the visible spectrum, *c* 1.6, H_2O).

Calcd. for $C_6H_{14}O_5$: C, 47.97; H, 9.39. Found: C, 47.69; H, 9.33.

Synthesis of Dimethylene-1,6-(*erythro*-3,4)-hexanetetrol.—1,6-*erythro*-3,4-Hexanetetrol (70 mg.) was formalated as described above for the preparation of 1,3:2,4:5,6-trimethylenesorbitol. Crystals separated on cooling the reaction mixture; yield 40 mg., m. p. 96–98° (uncor.). Pure material was obtained on further crystallization from ethanol; m. p. 97–98° (uncor.).

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.15; H, 8.10. Found: C, 55.27; H, 8.00.

Identification of Compound R as Dimethylene-allitol; Dimethylene-allitol Diacetate.[28]—Pure compound R pos-

(27) A. T. Ness, R. M. Hann and C. S. Hudson, THIS JOURNAL, **65**, 2215 (1943); *cf.* M. Schulz and B. Tollens, *Ann.*, **289**, 21 (1896).

(28) This compound had been isolated from product B (by the distillation of the formalated and acetylated material) by Dr. F. B. Moody of this Laboratory.

(29) Hydroxyl value was determined by acetylating *ca.* 74 mg. of the substance with 3 cc. of a 1:1 mixture of acetic anhydride–pyridine for forty-eight hours at room temperature. Water (25 cc.) was then added and after standing for four hours, the solution was titrated with 0.1 *N* alkali. A simultaneous blank was run. The hydroxyl value is expressed as cc. of 0.1 *N* alkali equivalent to the acetic acid required by 100 mg. of the sample.

(30) G. H. A. Clowes and B. Tollens, *Ber.*, **32**, 2841 (1899).

sessed the following constants on recrystallization from water: m. p. 258–259°, $[\alpha]^{25}$ 0° (throughout the visible spectrum, H_2O, 4-dm. tube). It was identified as dimethylene-allitol by comparison with a synthetic specimen (m. p. 256–257° mixed m. p. unchanged) of known structure prepared as described below.

Anal. Calcd. for $C_5H_{12}O_4(OH)_2$: C, 46.60; H, 6.85; hydroxyl value, 9.7 cc. 0.1 *N* NaOH per 100 mg. Found: C, 47.05; H, 6.87; hydroxyl value, 9.1 cc.

The substance was not oxidized by per-iodic acid.

Acetylation of compound R yielded a diacetate which on crystallization from 95% ethanol showed the constants: m. p. 177–178°, $[\alpha]^{25}$ 0° (*c*, 2.5, $CHCl_3$, throughout the visible spectrum). It gave no depression in m. p. on admixture with a synthetic specimen (m. p. 176–177°) of known structure prepared as described below.

Anal. Calcd. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found: C, 49.69; H, 6.24.

2,4:3,5-Dimethylene-allitol Di-*p*-toluenesulfonate.—An amount of 200 mg. of dimethylene-allitol (m. p. 256–257°) was suspended in 4.5 cc. of pyridine and 410 mg. of *p*-toluenesulfonyl chloride added. The mixture was heated at 90–95° for seventy-five minutes and then kept overnight at room temperature. The solution was filtered from a small amount of insoluble material and crystallization was effected by the addition of water; yield 180 mg., m. p. 185–193° (uncor.). Pure material was obtained on further crystallization from equal parts of acetic anhydride and acetic acid; m. p. 200.5–202°, six-sided plates.

Anal. Calcd. for $C_{22}H_{26}O_{10}S_2$: C, 51.35; H, 5.09; S, 12.46. Found: C, 51.55; H, 5.01; S, 12.44.

An amount of 71.1 mg. of the above substance, 150 mg. of sodium iodide and 3 cc. of acetone were heated in a sealed tube at 100° for 7.5 hours; wt. of sodium *p*-toluenesulfonate isolated, 45.2 mg. (1.7 moles per mole of starting material).

Synthesis of 2,4:3,5-Dimethylene-allitol and of 2,4:3,5-Dimethylene-allitol Diacetate.—An amount of 1.7 g. of *keto*-D-psicose pentaacetate[16b] was reduced with 1 g. of kieselguhr-supported nickel in 35 cc. of absolute ethanol under an initial hydrogen pressure of 1580 lb. per sq. in. (105 atm.) at 150° for four hours and then at 180° for three hours. The filtered solution yielded 0.9 g. of sirup after solvent removal. The sirup was saponified with barium hydroxide and the sirupy product (510 mg.) obtained after removal of barium ion with sulfuric acid, was formalated as described above (formalation procedure A) except that the formalation reaction mixture was heated to 95° over a twenty-minute period and held at that temperature for five minutes; yield 300 mg. (sirup). This sirup was dissolved in a small amount of 95% ethanol and crystals separated on standing at ice-box temperature; yield 10 mg., m. p. 256-257°.

An amount of 5 mg. of the above product was acetylated overnight at room temperature with 0.05 cc. each of pyridine and acetic anhydride. Crystallization ensued on the addition of a few drops of water to the reaction mixture; m. p. 176–177°.

Conversion of Compound R (2,4:3,5-Dimethylene-allitol) to Allitol and Allitol Hexaacetate.—An amount of 1.2 g. of compound R was deformalated according to the deformalation procedure B described above. The product was a sirup which deposited pure crystals from absolute ethanol solution; yield 40 mg., m. p. 148–149°. Wiemann[23] recorded for allitol a melting point of 149° and Steiger and Reichstein[16a] recorded 150–151° (cor.). From the mother liquor there was obtained D,L-(2,4-methylene-allitol), described below.

In another experiment, the crude product from the deformalation procedure was acetylated with acetic anhydride and sodium acetate under reflux to yield a crystalline acetate (from acetone–water); m. p. 61–62° (uncor.), $[\alpha]^{20}$ 0° ($CHCl_3$, throughout the visible spectrum). Wiemann[23] recorded the melting point of 61° for allitol hexaacetate.

Anal. Calcd. for $C_{18}H_{26}O_{12}$: C, 49.76; H, 6.03. Found: C, 50.28; H, 5.98.

D,L-**(2,4-Methylene-allitol).**—From the mother liquor of the above-described allitol crystallization there was isolated another crystalline substance that was obtained pure on further crystallization from absolute ethanol; yield 0.35 g., m. p. 138–139°. It was soluble in water; slightly so in ethanol; and was insoluble in acetone, ether and chloroform.

Anal. Calcd. for $C_7H_{10}O_2(OH)_4$: C, 43.30; H, 7.27; hydroxyl value, 20.6 cc. 0.1 *N* NaOH per 100 mg. Found: C, 43.31; H, 7.26; hydroxyl value, 20.7 cc.

Found on periodate oxidation (as moles per mole of substance): oxidant consumed, 1.0; formic acid, absent; formaldehyde, 1.1.

Isolation (as Dimethylene-2-desoxysorbitol Monolaurate) and Identification (as Dimethylene-2-desoxysorbitol Monoacetate) of 2-Desoxysorbitol; Dimethylene-allitol Dilaurate.—The aqueous solution (fraction III, Fig. 1) yielded on solvent removal 75 g. of dry, partially crystalline material. This was treated at room temperature for fourteen days with a solution of 135 g. of lauroyl chloride in 250 cc. of absolute chloroform and 130 cc. of anhydrous pyridine. The solution was then washed successively with *N* hydrochloric acid (total of 1 liter), water, saturated aqueous sodium bicarbonate–sodium chloride, and finally with water. It was then treated with "H Zeo-Carb,"[31] washed again with water, dried and concentrated under reduced pressure. During this concentration several crops of crystals were removed by filtration. The final chloroform filtrate yielded on solvent removal an amount of 147 g. of partially crystalline material which is under further investigation.

From the above crystalline material that separated on concentration of the chloroform solution there was obtained on further crystallization from absolute ethanol two pure substances: compound S, *ca.* 3 g., m. p. 108–109°, $[\alpha]^{25}$ 0° (*c* 3, $CHCl_3$, throughout the visible spectrum); and compound T, *ca.* 9 g., m. p. 77–78° (uncor.), $[\alpha]^{23}D$ −40.5° (*c* 2.2, $CHCl_3$), crystallizing in a spike-like form.

Anal. Compd. S: calcd. for $C_8H_{12}O_6(COC_{11}H_{23})_2$: C, 67.33; H, 10.24; $C_{11}H_{23}CO$, 3.50 cc. 0.1 *N* NaOH per 100 mg. Found: C, 67.24; H, 10.18; $C_{11}H_{23}CO$, 3.52 cc. Compd. T: calcd. for $C_8H_{13}O_5(COC_{11}H_{23})$: C, 64.49; H, 9.74; $C_{11}H_{23}CO$, 2.68 cc. 0.1 *N* NaOH per 100 mg. Found: C, 64.82; H, 9.77. $C_{11}H_{23}CO$, 2.72 cc.

Compound S exhibited the analytical data required by a dimethylene-hexitol dilaurate. It was identified as dimethylene-allitol dilaurate by conversion to the above-described dimethylene-allitol (identification by m. p. (258–259°) and mixed m. p.). Saponification was effected by alcoholic potash followed by neutralization with hydrochloric acid and concentration. The crystalline product separated on concentration and was removed by filtration.

Compound T yielded analytical data required for a dimethylene-desoxyhexitol monolaurate. It was soluble in ethanol, acetone, petroleum ether, ether and chloroform but was insoluble in water. It was identified as dimethylene-2-desoxysorbitol monolaurate by conversion to the dimethylene-2-desoxysorbitol monoacetate, described by Wolfrom, Moody, Konigsberg and Goepp.[1] To this end an amount of 1 g. of compound T was saponified with an excess of alcoholic potash. After concentration to 15 cc. and removal of some potassium laurate by filtration, the residue obtained on solvent removal was acetylated with acetic anhydride (2 cc.) and pyridine (2 cc.) and the water-insoluble acetate purified from 95% ethanol; m. p. 108–109°, mixed m. p. unchanged, $[\alpha]^{26}D$ −61.2° (*c* 1.8, $CHCl_3$). The previously recorded[1] constants for dimethylene-2-desoxysorbitol monoacetate are: m. p. 107.5–108° (uncor.), $[\alpha]^{26}D$ −61° (*c* 2.5, $CHCl_3$).

Isolation of a Dimethylenepentitol of Unknown Structure; Characterization of Its Monoacetate.—An amount of 40 g. of the material designated fraction M in our preceding communication[1] (*cf.* Fig. 1 of the preceding communication) was formalated as described above under formalation procedure A. The aqueous solution was concentrated to dryness under reduced pressure. This prod-

(31) A product of the Permutit Company, New York, N. Y.

uct was then extracted with chloroform, and the chloroform extract extracted with water. The water extract on concentration gave *ca.* 0.3 g. of dimethylene-allitol (compound **R**), which was removed by filtration. The filtrate was concentrated to dryness under reduced pressure to give 23 g. of sirup. From this sirup was obtained 0.4 g. of crystalline product, m. p. 139–141° from 95% ethanol, $[\alpha]^{25}D$ −47.4° (*c* 3.4, H_2O). Further purification from 95% ethanol did not alter these constants. The substance showed a strong tendency to separate as a gel from ethanol.

Anal. Calcd. for $C_7H_{11}O_4(OH)$: C, 47.72; H, 6.87; hydroxyl value,[29] 5.68 cc. 0.1 *N* NaOH per 100 mg.; mol. wt., 176.2. Found: C, 47.69; H, 6.82; hydroxyl value, 5.63 cc.; mol. wt. (Rast), 212.

The above analysis is in harmony with that required for a dimethylenepentitol. Crystalline D-arabitol was formalated according to formalation procedure B and the product was isolated as a sirup which did not crystallize on nucleation with the above substance.

The isolated dimethylenepentitol was further characterized as a monoacetate by acetylation with acetic anhydride and pyridine. Recrystallization from ethanol–water produced long rectangular crystals; m. p. 134–135°, insufficient material for polarization.

Anal. Calcd. for $C_9H_{14}O_6$: C, 49.54; H, 6.47. Found: C, 49.22; H, 6.23.

Preparation of 1-Desoxysorbitol (*syn.* L-Gulomethylitol) from 1-Desoxy-*keto*-D-fructose Tetraacetate.—An amount of 1.4 g. of 1-desoxy-*keto*-D-fructose tetraacetate[10] was dissolved in 25 cc. of absolute ethanol and 0.5 g. of kieselguhr-supported nickel catalyst added. The mixture was then hydrogenated at an initial pressure of 1290 lb. per sq. in. (86 atm.) of hydrogen at 150° for four hours and then at 170° for one hour. The filtered reaction mixture (non-reducing toward Fehling solution) was concentrated to dryness under reduced pressure; yield 1.2 g. (sirup). The product was acetylated at 90° for forty-five minutes with acetic anhydride (4.5 cc.) and twice-fused sodium acetate (0.2 g.). The cooled reaction mixture was poured into water and the solution nearly neutralized with sodium bicarbonate. A crystalline product separated on standing overnight at icebox temperature; yield 0.87 g. (55%), m. p. 101–102° (uncor.). Pure material was obtained on recrystallization from 95% ethanol; m. p. 105–106°, $[\alpha]^{27}D$ +22° (*c* 1.6, MeOH). For 1-desoxysorbitol pentaacetate, Gätzi and Reichstein[9] recorded the constants: m. p. 105–106° (cor.), $[\alpha]^{21}D$ +20.6 ± 2° (*c* 1.8, MeOH). 1-Desoxy-D-mannitol (*syn.* D-rhamnitol) pentaacetate is not known in crystalline condition and undoubtedly was present in the aqueous mother liquor.

An amount of 1.1 g. of 1-desoxysorbitol pentaacetate was saponified with barium hydrate (5.3 g. of barium hydroxide octahydrate in 53 cc. of water). Barium carbonate was precipitated by carbon dioxide and removed by filtration. Barium ion was removed in the filtrate with sulfuric acid and the filtered solution was concentrated to dryness; yield 0.49 g., m. p. 128–130°. Pure material was obtained on further crystallization from absolute ethanol–ether; m. p. 130–131°, $[\alpha]^{27}D$ +5° (*c* 1.7, H_2O). For 1-desoxysorbitol (*syn.* L-gulomethylitol), Müller and Reichstein[8] recorded the constants: m. p. 131–132°, $[\alpha]^{27}D$ +4° (*c* 4, H_2O).

Synthesis of Dimethylene-1-desoxysorbitol.—An amount of 0.38 g. of 1-desoxysorbitol was formalated as described above for the formalation of sorbitol except that the cooled formalation mixture was neutralized with sodium bicarbonate and concentrated to dryness under reduced pressure. The residue was extracted with chloroform to yield (on chloroform removal) a crystalline product. Pure material was obtained on further crystallization from absolute ethanol; yield 0.3 g., m. p. 116–117°, $[\alpha]^{26}D$ +23° (*c* 1.2, $CHCl_3$), needles.

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.57; H, 7.43. Found: C, 50.44; H, 7.27.

Solutions and sirups of various fractions of formalated product B were nucleated with crystals of this substance without success in identifying it as a component present.

Synthesis of Dimethylene-1-desoxysorbitol Monoacetate.—Acetylation of dimethylene-1-desoxysorbitol with acetic anhydride and pyridine yielded a crystalline product which on recrystallization from ethanol–water gave large needle-like crystals; m. p. 99–100°, insufficient material for polarization.

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 51.72; H, 6.95. Found: C, 51.70; H, 7.01.

Summary

1. By a combination of crystallization and extraction procedures, the following substances were found to be components of a commercial product manufactured by the electroreduction of D-glucose at *p*H 10–13 and below 30°: sorbitol, D-mannitol, allitol, a pentitol of unknown structure, 2-desoxysorbitol, and a 2-desoxyhexitol of undetermined configuration. Allitol and the unknown 2-desoxyhexitol were isolated in pure crystalline form; the other components were isolated in the form of pure, crystalline derivatives.

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

3. The following new crystalline derivatives of the isolated products have been described: dimethylene-2-desoxysorbitol monolaurate, dimethylene-allitol (its diacetate and dilaurate), D,L-(methylene-allitol), a dimethylenepentitol (unknown structure) and its monoacetate, a dimethylene-2-desoxyhexitol (configuration unknown), its monoacetate and monolaurate.

4. The placement of the methylene groups in dimethylene-allitol is shown to be 2,4:3,5, in verification of the prediction of Hann and Hudson, while that of methylene-allitol is demonstrated to be 2,4.

5. Procedures for the formalation and deformalation of sugar alcohols are described.

6. 1,6-(*erythro*-3,4)-Hexanetetrol and its dimethylene derivative have been prepared from *keto*-D-psicose pentaacetate.

7. 2,4:3,5-Dimethylene-allitol and its diacetate have been prepared from *keto*-D-psicose pentaacetate.

8. 1-Desoxysorbitol (its pentaacetate, dimethylene and dimethylene-monoacetate derivatives) have been prepared from 1-desoxy-*keto*-D-fructose tetraacetate.

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