164° and a specific rotation $[\alpha]^{20}D$ −9.7° in aqueous solution, these data being in agreement with those previously found for the 2,4-methylene-D-sorbitol obtained by the saponification of 1,6-diacetyl-3,5-di-(acetoxymethyl)-2,4-methylene-D-sorbitol (II). A mixed melting point determination with 2,4-methylene-D-sorbitol from this source showed no depression.

1,3:2,4:5,6-Trimethylene-D-sorbitol (I) from 1,3:2,4-Dimethylene-D-sorbitol (VI).—A solution of 1.0 g. of 1,3:2,4-dimethylene-D-sorbitol (VI) in a mixture of 1.0 cc. of concentrated hydrochloric acid and 1.0 cc. of 37% aqueous formaldehyde was warmed to 50°; within thirty minutes crystallization of needles was noted and after forty-eight hours the mixture was cooled to 5°. the needles were separated by filtration, washed with ice-cold 50% alcohol, and dried. The yield was 0.90 g. (85%). The product, after recrystallization from 20 parts of 50% alcohol, showed a melting point of 210–214° and a mixed melting point determination with authentic trimethylene-D-sorbitol showed no depression.

Summary

The condensation of D-sorbitol with formaldehyde under the influence of concentrated hydrochloric acid yields, in addition to the known trimethylene-D-sorbitol of Schulz and Tollens, a new crystalline dimethylene-D-sorbitol. The limited acetolysis of the known trimethylene-D-sorbitol yields a diacetyl-di-(acetoxymethyl)-methylene-hexitol, which upon saponification is transformed into a crystalline methylene-D-sorbitol that can be only 2,4-methylene-D-sorbitol since it is converted by periodate oxidation and subsequent reduction to 2,4-methylene-xylitol of proved structure.

The new dimethylene-D-sorbitol can be only 1,3:2,4-dimethylene-D-sorbitol since upon periodate oxidation it yields an *aldehydo*-2,4:3,5-dimethylene-L-xylose which is successively converted to 2,4:3,5-dimethylene-L-xylitol, 1,5-diacetyl-3-acetoxymethyl-2,4-methylene-xylitol and 2,4-methylene-xylitol by known reactions.

The fact that the limited acetolysis of 2,4:3,5-dimethylene-L-xylitol forms a compound of *meso* structure rather than one possessing optical activity is cited as evidence supporting the previously proposed acetolysis mechanism based on the hypothesis that the acetal linkages of methylene acetals which are formed through primary alcoholic groups are more easily ruptured than those formed through secondary alcoholic groups; this experimental corroboration allows assignment of the structures of 1,6-diacetyl-3,5-di-(acetoxymethyl)-2,4-methylene-D-sorbitol and 1,5,6-triacetyl-3-(acetoxymethyl)-2,4-methylene-D-sorbitol, respectively, to the acetolysis products of trimethylene-D-sorbitol and 1,3:2,4-dimethylene-D-sorbitol.

In view of the present experimental results, and particularly the conclusive establishment of the presence of the 2,4-acetal linkage, it seems highly probable that the trimethylene-D-sorbitol of Schulz and Tollens is 1,3:2,4:5,6-trimethylene-D-sorbitol, the rare C_5O_2 dioxepane ring that is present in 1,3:2,5:4,6-trimethylene-D-mannitol being absent from the structure of the isomeric trimethylene-D-sorbitol.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

2,4:3,5-Dimethylene-D,L-xylitol and 2,4-Methylene-xylitol

BY RAYMOND M. HANN, A. T. NESS AND C. S. HUDSON

In the course of the study of the acetolysis of trimethylene-D-sorbitol that is described in the accompanying article[1] there was obtained by degradative reactions a monomethylene-pentitol (m. p. 108–109°) the structure and configuration of which needed to be established. In configuration it is limited to a monomethylene derivative of xylitol or D-arabitol by reason of its origin. In aqueous solution no optical rotation was detected, which indicated the probability that the compound is a monomethylene-xylitol of *meso* structure since all structures for a monomethylene-D-arabitol represent optically active systems. The direct identification of its constituent pentitol through acid hydrolysis seemed of little attraction because of the experimental difficulties that are often encountered in attempts to hydrolyze methylene cyclic acetals. Accordingly, it was sought to produce the substance by condensing formaldehyde with xylitol, a procedure which, if successful, would establish the identity of its constituent pentitol and might also lead to a less laborious method for obtaining it.

There appears to be no recorded combination of formaldehyde with xylitol, although dibenzylidene[2] and di-isopropylidene xylitols[3] are known. A crystalline dimethylene-xylitol (m. p. 201–202°) was obtained in 91% yield by the reaction of xylitol with 37% aqueous formaldehyde and concentrated hydrochloric acid for two hours at 50°. One of the methylene groups in this dimethylene-xylitol is readily removable, as will be described, and the resulting monomethylene-xylitol proved to be identical with the monomethylene-pentitol (m. p. 108–109°) which was obtained from trimethylene-D-sorbitol. This monomethylene-xylitol does not react with sodium periodate and thus it contains no α-glycol group;

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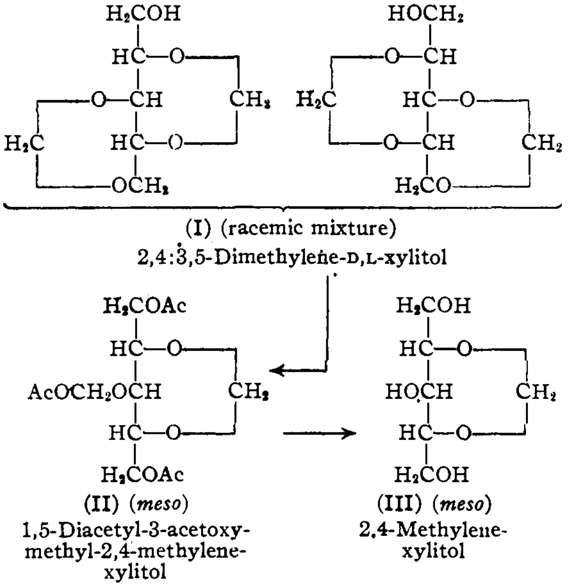
[1] Ness, Hann and Hudson, THIS JOURNAL, **66**, 665 (1944).

[2] (a) L. de Bruyn and van Ekenstein, *Rec. trav. chim.*, **18**, 151 (1899); (b) Wolfrom and Kohn, THIS JOURNAL, **64**, 1739 (1942).

[3] (a) Tipson and Cretcher, *J. Org. Chem.*, **8**, 95 (1943); (b) Hann, Ness and Hudson, THIS JOURNAL, **66**, 73 (1944).

the only possible structure for the acetal is therefore that of 2,4-methylene-xylitol (III). Its optical inactivity is to be ascribed to its *meso* configuration.

Consider next the structure of the dimethylene-xylitol. Obviously the substance contains one free hydroxyl group and it readily formed crystalline mono acetyl, benzoyl, carbanilo and tosyl derivatives. The tosyl-dimethylene-xylitol reacted with a solution of sodium iodide in acetonylacetone to yield a crystalline iodo-dimethylene-xylitol which was reduced by hydrogen and Raney nickel to a desoxy-dimethylene-xylitol; the replacement of the tosyl group by the iodine atom is a strong indication, by the Oldham-Rutherford rule,[4] that it is attached at a terminal carbon atom. Conclusive proof of this inference was obtained when it was found that the desoxy-dimethylene-xylitol is identical with the desoxy-dimethylene-xylitol that is obtained by heating the known 1-desoxy-2,3,4,5-di-isopropylidene-D,L-xylitol[3b] with formaldehyde and concentrated hydrochloric acid. The substance can be only 1-desoxy-2,3,4,5-dimethylene-D, L-xylitol and the diacetal from which it is derived must be a 2,3,4,5-dimethylene-D,L-xylitol. The allocation of the acetal linkages among the four positions in its structure was made through the acetolysis reaction previously applied by us to trimethylene-D-mannitol.[5] Upon limited acetolysis in a one per cent. sulfuric acid mixture at about 0° the 2,3,4,5-dimethylene-D,L-xylitol is converted in 44% yield to a crystalline substance which had the composition of a diacetyl-acetoxymethyl-methylene-xylitol; upon saponification with sodium methylate the latter compound is converted in nearly quantitative yield to the previously mentioned 2,4-methylene-xylitol (III), originally obtained from trimethylene-D-sorbitol. The 2,3,4,5-dimethylene-D,L-xylitol from which it was formed must be 2,4:3,5-dimethylene-D,L-xylitol (I) and its acetolysis product is in all probability 1,5-diacetyl-3-acetoxymethyl-2,4-methylene-xylitol (II), a *meso* structure.



(I) (racemic mixture)
2,4:3,5-Dimethylene-D,L-xylitol

(II) (*meso*)
1,5-Diacetyl-3-acetoxymethyl-2,4-methylene-xylitol

(III) (*meso*)
2,4-Methylene-xylitol

We express our appreciation to Mr. George L. Keenan of the Food and Drug Administration, Federal Security Agency, for the determination of the optical crystallographic properties of the 2,4:3,5-dimethylene-L- and D,L-xylitols and their acetyl derivatives.

Experimental

2,4:3,5-Dimethylene-D,L-xylitol (I).—A solution of 5.0 g. of crystalline xylitol in a mixture of 5 cc. of concentrated hydrochloric acid and 5 cc. of 37% formaldehyde was allowed to stand at 50° for two hours; the magma which formed when the reaction mixture was cooled to room temperature was thinned with 25 cc. of alcohol and the precipitate (5.1 g.) was separated by filtration; the mother liquor was evaporated by an air current and the residual solid was crystallized from 10 cc. of alcohol to yield an additional 0.2 g. of product, making the total yield 91%. The colorless compound was recrystallized by solution in 3 parts of warm water and the addition of 15 parts of alcohol, and obtained as small thin lath-like crystals with a m. p. of 201–202°.[6] It is soluble in cold pyridine, warm methyl and ethyl alcohols and acetic acid, and insoluble in acetone, chloroform and benzene. At 24° a saturated aqueous solution contains 4.2 g. of the substance in 100 cc. of solution; a saturated aqueous solution of 2,4:3,5-dimethylene-L-xylitol at 24° contains 3.7 g. of the acetal in 100 cc. of solution. Thus the D,L-form is more soluble than the L-form but less than twice its solubility. The substance appears to belong to the class of compounds which have been defined by Kipping and Pope[7] as pseudo racemates. An optical crystallographic comparison of it and the previously described L-form [m. p. 217–219°; $[\alpha]^{20}_{D}$ −25.3° in water] was made by Mr. George L. Keenan who reported as follows:

"In ordinary light (plane polarized) both substances were seen to consist of elongated rods and prisms. The L-form showed prism faces that were straight and parallel, while the D,L-compound showed many of the prisms to be somewhat fibrous and curved. In parallel polarized light (crossed nicols) the extinction was parallel and the sign of elongation negative for both compounds. The n_α, n_β, and n_γ refractive indices were identical in both compounds. However, in the case of the authentic L-compound the prisms are so oriented that the n_α and n_β values are commonly shown, while in the D,L-compound n_α and n_γ are commonly shown. Interference figures were not observed on either compound. As a result of the examination, these compounds are very similar if not identical optically. The most striking feature for differentiation is the difference in orientation. The indices are as follows:

	D,L-Compound	L-Compound
n_α	1.524	1.524
n_β	1.543	1.544
n_γ	1.560	1.558"

The melting point of the D,L-form was depressed upon admixture of a small amount of the L-form and the L-form did not dissolve in a saturated aqueous solution of the D,L-form. Although an exhaustive study was not undertaken, the experiments cited above agree in their indication that

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(4) Oldham and Rutherford, This Journal, 54, 366 (1932); Oldham, *J. Chem. Soc.*, 127, 2840 (1925).

(5) Ness, Hann and Hudson, This Journal, 65, 2215 (1943).

(6) All of the crystalline compounds described in the experimental part were recrystallized to constant melting point; all melting points were determined with the stem of the calibrated thermometer immersed in the rapidly stirred bath.

(7) Kipping and Pope, *J. Chem. Soc.*, 71, 989 (1897).

2,4:3,5-dimethylene-D,L-xylitol is a pseudo rather than a true racemate; its crystals are comparable with those from a solution of two isomorphous substances.

Anal. Calcd. for $C_7H_{12}O_5$: C, 47.72; H, 6.87. Found: C, 47.61; H, 6.93.

1-Acetyl-2,4:3,5-dimethylene-D,L-xylitol.—A mixture of 4.4 g. of 2,4:3,5-dimethylene-D,L-xylitol, 0.5 g. of fused sodium acetate and 22.5 cc. of acetic anhydride was heated gently and, following a vigorous exothermic reaction, refluxed for fifteen minutes; upon pouring the cooled reaction mixture into 25 cc. of water, 3.4 g. of the acetate crystallized, and an additional 2.0 g. was obtained by concentration of the acetic acid filtrate, making the yield quantitative. The compound was recrystallized from 20 parts of boiling water in the form of needles which melted at 156–157° and showed no rotation in chloroform solution. (*c*, 0.5). It can also be recrystallized from 10 parts of methyl or ethyl alcohol and is readily soluble in acetone, chloroform and benzene. The compound is a true racemate; a mixed melting point with a small amount of the previously described 1-acetyl-2,4:3,5-dimethylene-L-xylitol (m. p. 153–154°) gave a depressed value of 146–156°; an optical crystallographic examination by Mr. Keenan showed that in parallel polarized light (crossed nicols) the extinction was parallel and the elongation negative, the indices of refraction being $n_\alpha = 1.495$, $n_\beta = 1.514$ and $n_\gamma = 1.539$ (all ±0.002), these values being distinctly different from those of 1-acetyl-2,4:3,5-dimethylene-L-xylitol.[1] The substance is therefore to be classed as a true racemate.

Anal. Calcd. for $C_9H_{14}O_6$: C, 49.54; H, 6.47; CH_3CO, 19.7. Found: C, 49.66; H, 6.47; CH_3CO, 19.5.

1-Benzoyl-2,4:3,5-dimethylene-D,L-xylitol.—This compound was obtained in a yield of 88% (2.8 g.) by the benzoylation of 2,4:3,5-dimethylene-D,L-xylitol (2.0 g.) in pyridine solution with benzoyl chloride. It was recrystallized from 30 parts of alcohol and obtained in the form of fine needles which melted at 164–165°. The substance is soluble in acetone, methyl alcohol, chloroform and ethyl acetate and insoluble in water.

Anal. Calcd. for $C_{14}H_{16}O_6$: C, 60.00; H, 5.75; C_6H_5CO, 37.5. Found: C, 60.35; H, 5.79; C_6H_5CO, 37.2.

1-Carbanilo-2,4:3,5-dimethylene-D,L-xylitol.—This derivative was prepared by a procedure similar to that which Wolfrom and Pletcher[8] have employed for the preparation of the carbanilates of sugar glycosides. A mixture of 2.0 g. of 2,4:3,5-dimethylene-D,L-xylitol, 1.4 cc. of phenyl isocyanate and 20 cc. of pyridine was boiled for two hours under a reflux condenser protected from atmospheric moisture by a drying tube. The carbanilo derivative (1.2 g.) which precipitated from the solution on cooling was recrystallized from 20 parts of acetone as clusters of glistening prisms which melted at 196–197°. An additional 2.0 g. of compound showing the same melting point was obtained by allowing the pyridine to evaporate from the mother liquor and recrystallizing the residue from acetone. The total yield was 94%. The substance is readily soluble in warm methyl and ethyl alcohols, chloroform and dioxane, sparingly soluble in warm water and practically insoluble in cold water and benzene.

Anal. Calcd. for $C_{14}H_{17}O_6N$: C, 56.94; H, 5.80; N, 4.74. Found: C, 56.98; H, 5.64; N, 4.64.

1-Tosyl-2,4:3,5-dimethylene-D,L-xylitol.—A mixture of 1.0 g. of 2,4:3,5-dimethylene-D,L-xylitol, 1.2 g. (1.1 molecular equivalents) of *p*-toluenesulfonyl chloride and 10 cc. of pyridine was agitated at room temperature until the diacetal dissolved (four hours) and the resulting solution was allowed to stand for eighteen hours and then was poured upon crushed ice. The precipitated tosyl derivative (1.7 g., 90%) was recrystallized from 20 parts of alcohol and formed prisms which melted at 145–146°. The compound is readily soluble in cold chloroform and acetone, methyl alcohol, warm benzene and dioxane and insoluble in water.

Anal. Calcd. for $C_{14}H_{18}O_7S$: C, 50.90; H, 5.49; S, 9.70. Found: C, 50.92; H, 5.48; S, 9.58.

1-Iodo-2,4:3,5-dimethylene-D,L-xylitol.—The replacement of the tosyl group of 1-tosyl-2,4:3,5-dimethylene-D,L-xylitol by iodine was incomplete in an experiment in which 5.0 g. of the tosyl derivative, 5.0 g. of sodium iodide and 100 cc. of acetone were heated at 100° for four hours; only about 50% of the sodium *p*-toluenesulfonate which would be expected from the removal of the tosyl group precipitated in the acetone solution and the product, which melted from 119 to 130°, was a mixture of unchanged tosyl derivative and some of the desired 1-iodo-2,4:3,5-dimethylene-D,L-xylitol. A quantitative conversion was attained however by substitution of acetonylacetone (25 cc.) as a solvent[9] and carrying out the reaction at 120° for four hours or by refluxing the reactants in acetic anhydride (25 cc.) for one hour. The 1-iodo-2,4:3,5-dimethylene-D,L-xylitol deposited from its solution in 15 parts of alcohol in the form of needles which melted at 144–145°; a mixed melting point determination with 1-tosyl-2,4:3,5-dimethylene-D,L-xylitol, which melts at 145–146°, gave a value of 117–119°. The iodo derivative is readily soluble in cold acetone and chloroform and in warm methyl and ethyl alcohols and is insoluble in water.

Anal. Calcd. for $C_7H_{11}O_4I$: C, 29.39; H, 3.88; I, 44.36. Found: C, 29.39; H, 3.84; I, 44.28.

1-Desoxy-2,4:3,5-dimethylene-D,L-xylitol from 1-Iodo-2,4:3,5-dimethylene-D,L-xylitol.—To a solution of 3.0 g. of 1-iodo-2,4:3,5-dimethylene-D,L-xylitol in 150 cc. of methyl alcohol, 3 cc. of 20% methyl alcoholic potassium hydroxide solution and 2.0 g. of Raney nickel were added and the reaction mixture was agitated vigorously at 22° while hydrogen under a slight positive pressure was introduced. In thirty minutes 240 cc. (theory, 235 cc., S. T. P.) of hydrogen was taken up and only 5 cc. more was absorbed in a further thirty minutes. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo* to dryness. The solid was extracted with 20 cc. of boiling absolute alcohol and, upon cooling the extract, the desoxy diacetal crystallized in the form of fine needles; the compound, after recrystallization from 15 parts of alcohol, melted at 155–156°, and the value was not altered by further recrystallization; it is readily soluble in acetone, warm methyl alcohol and warm water, and relatively insoluble in cold water. The substance sublimes readily. The yield was 1.3 g. (76%).

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.59; H, 7.60.

1-Desoxy-2,4:3,5-dimethylene-D,L-xylitol from 1-Desoxy-2,3,4,5-di-isopropylidene-D,L-xylitol.[3b]—A solution of 1.5 g. of 1-desoxy-2,3,4,5-di-isopropylidene-D,L-xylitol in a mixture of 2 cc. of 37% aqueous formaldehyde and 2 cc. of concentrated hydrochloric acid was allowed to stand for two and one-half hours at 50°; the solution was diluted with 25 cc. of alcohol and concentrated *in vacuo* to a sirupy residue; following the addition of 2.0 g. of barium carbonate, the residue was dried by thes uccessive addition and evaporation of two 25 cc. portions of absolute alcohol and finally extracted with warm absolute alcohol The extract, upon removal of the solvent, deposited fine needles (m. p. 148–152°) which, after one recrystallization from 20 parts of absolute alcohol, melted at 155–156°; a mixed melting point determination with the 1-desoxy-2,4:3,5-dimethylene-D,L-xylitol described in the preceding paragraph also gave 155–156°. The yield was moderate, 0.30 g. (37%), presumably because of the volatile nature of the product.

1,5-Diacetyl-3-acetoxymethyl-2,4-methylene-xylitol (II).—To an ice-cold suspension of 1.0 g. of 2,4:3,5-dimethylene-D,L-xylitol in a mixture of 7 cc. of acetic anhydride and 3 cc. of glacial acetic acid was added 10 cc. of an ice-cold acetylating solution (prepared by adding 2 cc. of concentrated sulfuric acid dropwise to an ice-cold mixture of 70 cc. of acetic anhydride and 30 cc. of acetic acid); the diacetal dissolved and after standing for fifteen minutes at 5° the reaction mixture was poured upon crushed ice.

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(8) Wolfrom and Pletcher, This Journal, **62**, 1151 (1940).

(9) Murray and Purves, *ibid.*, **62**, 3195 (1940).

The crystalline precipitate (0.3 g., m. p. 137°) was separated by filtration and the filtrate was neutralized with sodium bicarbonate and extracted with chloroform; the chloroform was evaporated and the sirupy residue remaining was crystallized from 10 cc. of hot water and yielded a further 0.5 g. of product melting at 137–138° making the yield of 1,5-diacetyl-3-acetoxymethyl-2,4-methylene-xylitol 44%; a residual sirup (0.5 g.) could not be induced to crystallize. The substance is readily soluble in cold methyl and ethyl alcohols, chloroform, acetone and benzene. It deposited from its solution in 30 parts of water as long needles which melted at 138–139°.

Anal. Calcd. for $C_{13}H_{20}O_9$: C, 48.75; H, 6.29; saponification, 0.1117 g. substance requires 10.46 cc. 0.1 *N* NaOH (3 saponifiable groups). Found: C, 48.85; H, 6.34; saponification, 0.1117 g. substance consumed 10.32 cc. 0.1 *N* NaOH.

2,4-Methylene-xylitol (III) from 1,5-Diacetyl-3-acetoxymethyl-2,4-methylene-xylitol (II).—A solution of 1.6 g. of 1,5-diacetyl-3-acetoxymethyl-2,4-methylene-xylitol in 15 cc. of chloroform was cooled to 0° and 1 cc. of 0.1 *N* sodium methylate solution was added. The next day the chloroform was evaporated by an air current and the sirup which remained was dissolved in 2 cc. of warm alcohol; the reaction product (0.7 g., 88%), which crystallized as the solution cooled, was recrystallized from 12 parts of alcohol as elongated prisms which melted at 108–109°. It is readily soluble in water, warm methyl and ethyl alcohols, and dioxane and relatively insoluble in benzene, acetone and chloroform.

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 43.98; H, 7.40.

Triacyl Derivatives of 2,4-Methylene-xylitol (III) (a) 1,3,5-Triacetyl-2,4-methylene-xylitol was obtained in nearly quantitative yield (1.7 g.) by acetylation of the acetal (1.0 g.) in pyridine solution with acetic anhydride. It was recrystallized from 5 parts of alcohol as long needles which melted at 87–88°. It is readily soluble in acetic acid, acetone, chloroform and ethyl acetate and nearly insoluble in water.

Anal. Calcd. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25; CH_3CO, 44.5. Found: C, 49.69; H, 6.19; CH_3CO, 44.5.

(**b**) The **1,3,5-tribenzoyl-2,4-methylene-xylitol** (2.9 g., quantitative) which was obtained by the benzoylation of 1.0 g. of 2,4-methylene-xylitol in pyridine solution by benzoyl chloride (2.5 cc.) was recrystallized from 20 parts of alcohol and obtained in the form of needles which melted at 117–118°. The substance is soluble in cold chloroform, ethyl acetate and acetone, warm methyl and ethyl alcohols and insoluble in water.

Anal. Calcd. for $C_{27}H_{24}O_8$: C, 68.06; H, 5.08; C_6H_5CO, 66.2. Found: C, 68.16; H, 5.25; C_6H_5CO, 66.2.

(**c**) An ice-cold solution of 2.0 g. of 2,4-methylene-xylitol in 10 cc. of pyridine was mixed with a cold solution of 9.0 g. of *p*-toluenesulfonyl chloride in 15 cc. of pyridine and the mixture was allowed to stand at 20° for forty-eight hours. The **1,3,5,tritosyl-2,4-methylene-xylitol** (7.7 g.) which precipitated upon pouring the mixture upon crushed ice was recrystallized from 20 parts of 1:1 dioxane-alcohol as fine needles which melted at 198–199°. The compound is difficultly soluble in the usual organic solvents.

Anal. Calcd. for $C_{27}H_{30}O_{11}S_3$: C, 51.74; H, 4.83; S, 15.35. Found: C, 51.76; H, 4.89; S, 15.26.

1,5-Dibenzoyl-2,4-methylene-xylitol.—A solution of 1.0 g. of 2,4-methylene-xylitol in 10 cc. of pyridine was cooled in ice and to the stirred solution 1.4 cc. of benzoyl chloride (2 molecular equivalents) was added dropwise. After standing for two hours at 25° the mixture was poured upon crushed ice and the crystalline precipitate (1.3 g., 56%) was recrystallized from 20 parts of alcohol; the small needles so obtained showed a melting point of 139–140°; the substance is soluble in chloroform, pyridine and acetone and insoluble in water. The 1 and 5 positions for the benzoyl groups are assigned because of the well-known preferential benzoylation of primary hydroxyl groups under these experimental conditions; thus D-arabitol yields 1,5-dibenzoyl-D-arabitol,[10] the structure of which has been proved conclusively.

Anal. Calcd. for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41; C_6H_5CO, 56.5. Found: C, 64.72; H, 5.34; C_6H_5CO, 55.9.

Stability of 2,4-Methylene-xylitol (III) against Oxidation by Sodium Periodate.—To a solution of 0.2032 g. of 2,4-methylene-xylitol in 10 cc. of water at 25°, 6.30 cc. of 0.432 *M* sodium periodate was added and the volume was adjusted to 25 cc. with water. Analysis of 5 cc. subsamples at the expiration of one and forty-eight hours showed that none of the sodium periodate had been consumed. The failure of this reagent to oxidize the 2,4-methylene-xylitol indicates that its structure does not include a glycol grouping. The only possible structure for a monoacetal of a pentitol which conforms with this limitation is that of a 2,4-acetal; methylene-xylitol is therefore 2,4-methylene-xylitol.

Summary

The isolation and proof of structure of 2,4:3,5-dimethylene-D,L-xylitol and 2,4-methylene-xylitol are described. The diacetal must be a 2,3,4,5-dimethylene-D,L-xylitol because its monotosyl derivative is converted to an iodo derivative which is reduced by hydrogen and Raney nickel to a desoxy-dimethylene-D,L-xylitol and this desoxy compound is identical with the 1-desoxy-2,3,4,5-dimethylene-D,L-xylitol that is obtained by treating the known 1-desoxy-2,3,4,5-di-isopropylidene-D,L-xylitol with formaldehyde and concentrated hydrochloric acid. The acetal linkages must be at positions 2,4 and 3,5 of the xylitol moiety because the saponification of the acetolysis product of the diacetal, namely, 1,5-diacetyl-3-acetoxymethyl-2,4-methylene-xylitol, yields a monomethylene-xylitol which is not oxidized by glycol-splitting reagents; this fact not only limits its structure to that of 2,4-methylene-xylitol but also proves that the structure of the dimethylene-D,L-xylitol from which it is derived must be that of 2,4:3,5-dimethylene-D,L-xylitol.

The experimental findings confirm and extend the previously published views regarding the limited acetolysis of the methylene acetals of the sugar alcohols.

BETHESDA, MARYLAND RECEIVED JANUARY 21, 1944

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[10] Haskins, Hann and Hudson, THIS JOURNAL, **65**, 1664 (1943).