

The acetal grouping of the dimethylene-L-rhamnitol which is attacked by the acetolyzing solution is shown to be attached to the 1,3-positions of the L-rhamnitol moiety by proof (1) of the absence of a primary hydroxyl group in the dimethylene-L-rhamnitol molecule and (2) by the preparation from it of 1,3:2,5-dimethylene-4-methyl-L-rhamnitol which proves to be the enantiomorph of 1,3:2,5-dimethylene-4-methyl-D-rhamnitol prepared by the condensation of formaldehyde with 4-methyl-D-rhamnitol that is ob-

tained by a series of standard reactions from authentic methyl 4-methyl- α -D-mannopyranoside.

The application to L-rhamnitol of the generalizations relating the structures and configurations of the methylene and benzylidene acetals of polyhydric alcohols indicates that in the case of rhamnitol a 1,3:2,5 acetal structure is to be expected; the experimental results bear out this prediction.

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[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY, ALBANY, CALIFORNIA¹]

1,4-Anhydro-D,L-xylitol

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In a study of the reactions of xylitol, its dehydration with acid catalysts has been investigated. Although the preparation of anhydro derivatives of the hexitols, sorbitol, mannitol and dulcitol has been studied by a number of investigators, the corresponding reaction with the pentitols has received very little attention.²

By dehydrating xylitol with sulfuric acid or benzenesulfonic acid, a pure optically inactive anhydroxylitol has been isolated in crystalline form and its structure determined. The results of periodate oxidation have shown that the new product obtained by the removal of one molecule of water from xylitol must contain a 1,4 oxygen bridge. Because of the meso configuration of xylitol, anhydroxylitol must exist as a racemic mixture and is accordingly named 1,4-anhydro-D,L-xylitol.

Xylitol on heating with 1% sulfuric or benzenesulfonic acid at 145–160° for forty to fifty minutes yielded a mixture of dehydration products from which anhydroxylitol could be separated by evaporative distillation *in vacuo* in a short-path still in yields of 65%. Anhydroxylitol has been characterized by the preparation of three crystalline derivatives, the tribenzoate, the monotrityl diacetate and the tricarbanilate. Refluxing the tricarbanilate with barium methylate in methanol regenerated the original anhydroxylitol. This procedure has been found useful for isolating the pure compound from mixtures. Anhydroxylitol, first obtained as a viscous sirup, crystallized very slowly under anhydrous conditions and was recrystallized from mixtures of isoamyl alcohol and diethyl ether. The crystals were very hygroscopic and became sirupy after a few minutes of exposure to the atmosphere.

(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) The Alien Property Custodian has made public the patent application A. P. C. No. 367,300 of Felix Grandel, describing the dehydration of xylitol with acids and salts to yield mixtures of mono- and dianhydroxylitol.

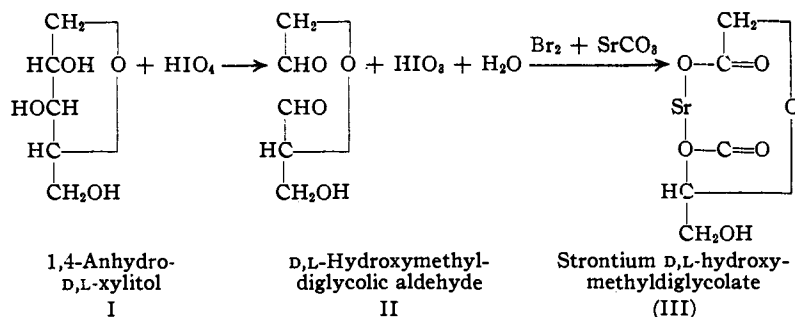
When an aqueous solution of anhydroxylitol (I)³ was oxidized with sodium metaperiodate, one molecular equivalent of oxidant was consumed and no formic acid or formaldehyde was produced. Reaction with periodic acid likewise consumed one equivalent of oxidant. The presumed dialdehyde (II) on further oxidation with bromine water in the presence of strontium carbonate yielded the strontium salt (III). Analyses of this salt showed it to be one of a dicarboxylic acid of five carbon atoms. The salt named in accordance with established terminology⁴ is strontium D,L-hydroxymethyldiglycolate.

The consumption of one equivalent of periodic acid requires that two of the three hydroxyl groups must be adjacent and the absence of formaldehyde shows that both glycol hydroxyl groups must be secondary. The only structures satisfying these conditions would be a 1,4- or a 2,5-anhydroxylitol which constitute an enantiomorphous pair. Anhydroxylitol and its derivatives were found to be optically inactive. The assigned structure is conclusively proved by the isolation of the strontium salt (III) from the oxidation product of anhydroxylitol. The preparation of a monotrityl diacetyl derivative furnishes supporting evidence for a structure containing one primary hydroxyl group. The designation of the new compound as an anhydroxylitol is dependent on the reasonable assumption that no inversion of configuration occurs during dehydration. A Walden inversion occurring at the point of attachment of the oxygen ring would lead to a racemate of 1,4-anhydro-D- and -L-arabitol. It has been shown that in the analogous dehydration of sorbitol⁵ no Walden inversion takes place. The formation of 1,4 oxygen rings has been observed in the dehydration of hexitols as sorbitol which on heat-

(3) In the formulas only the D members of the D,L pairs are shown.

(4) Jackson and Hudson, *THIS JOURNAL*, **59**, 994 (1937).

(5) Hockett, Abstract of Paper, 105th meeting, American Chemical Society, Detroit, Michigan, April, 1943.



ing with sulfuric acid yields 1,4-anhydrosorbitol⁶ and can be dehydrated further to 1,4:3,6-dianhydrosorbitol.⁶

Experimental

Dehydration of Xylitol.—Eighty grams of crystalline xylitol and 0.8 g. of benzenesulfonic acid were heated together in a 500-ml. round-bottom flask for forty-five minutes at 155–160° while a slow stream of nitrogen was bubbled through the melt to assist in mixing and removal of water. The dark viscous liquid was dissolved in 400 ml. of water, decolorized with Darco G60 and freed from benzenesulfonic acid by percolating through a 50 cc. column of an acid-absorbing resin (Amberlite IR-4⁷) to yield a solution essentially free of acid (pH 5.0). The solution was concentrated *in vacuo* at 40–45° to a dry sirup weighing 61 g. For isolation of anhydroxylitol the sirup was evaporatively distilled in a short path still of a type described by Matchett and Levine⁸ at 0.01 mm. and a bath temperature of 145–165° to yield 45.5 g. (over-all yield from xylitol, 65%) of colorless distillate, n_D^{20} 1.4980. The residue in the still was a very viscous material which could not be distilled without excessive decomposition. The product was again distilled in the same manner to yield pure sirupy anhydroxylitol, n_D^{20} 1.4977, d_4^{25} 1.354. *Anal.* Calcd. for C₅H₁₀O₄: C, 44.77; H, 7.5. Found: C, 44.60; H, 7.6. After standing for one year under anhydrous conditions, the sirup crystallized. Anhydroxylitol was recrystallized by dissolving in 5 parts of warm isomyl alcohol, cooling slowly to 0°, and adding small quantities of absolute ether to the cold solution over a period of several days until five volumes of ether had been added. The supernatant liquid was poured off and the mass of small triangular crystals was washed three times with small portions of absolute ether and dried *in vacuo* at room temperature for several days; m. p. 37–38°, *Anal.* Calcd. for C₅H₁₀O₄: C, 44.77; H, 7.5. Found: C, 44.5; H, 7.53. The crystalline anhydroxylitol is extremely hygroscopic. It is soluble in water, pyridine, and the lower alcohols, and is insoluble in ether, chloroform and hydrocarbons. Substitution of sulfuric acid for benzenesulfonic acid in the dehydration gave somewhat lower yields due to excessive charring of the xylitol.

Anhydroxylitol Tricarbanilate.—This derivative was prepared according to the procedure of Wolfrom and Pletcher.⁹ A solution of 4.0 g. (0.03 mole) of anhydroxylitol and 12.6 ml. (0.106 mole) of phenyl isocyanate in 50 ml. of dry pyridine was refluxed under anhydrous conditions for two hours. The product was precipitated as an oil by the addition of 400 ml. of petroleum ether (Skellysolve B) and the supernatant liquid was decanted. The oil was washed twice by decantation with 100-ml. portions of petroleum ether to remove excess phenyl isocyanate and

pyridine and on trituration with 200 ml. of absolute ether crystallized to yield 12.5 g. (85%) of white fibrous crystals, m. p. 185–189°. Concentration of the mother liquor yielded a small second crop of the derivative. One recrystallization from 200 ml. of absolute ethanol yielded the pure tricarbanilate, m. p. 193–194.5° (cor.). *Anal.* Calcd. for C₂₅H₂₈O₇N₃: C, 63.54; N, 8.55; H, 5.13. Found: C, 63.8; N, 8.5; H, 5.3.

Regeneration of Anhydroxylitol from the Tricarbanilate.

—The procedure used was a modification of the method of Salmon and Powell.¹⁰ A mixture of 72 g. of anhydroxylitol tricarbanilate, 1,000 ml. of absolute methanol and 100 ml. of 0.61 *N* barium methylate-methanol solution was refluxed under anhydrous conditions for three hours, the tricarbanilate going into solution after an hour of refluxing. The cooled solution was exactly neutralized with normal sulfuric acid and two liters of water was added to precipitate the methylphenylurethan. After filtration, the solution was concentrated to 1,000 ml. and was filtered from methylphenylurethan which had crystallized. The last traces of methylphenylurethan were removed by extracting five times with 150-ml. portions of ether followed by one extraction with 200 ml. of Skellysolve B. Cations and anions were completely removed from the solution by successive passage through a column of Amberlite IR-100⁷ (hydrogen cycle) and Amberlite IR-4,⁷ respectively. The solution was then concentrated *in vacuo* to a dry sirup and evaporatively distilled in a short-path still at 0.02 mm. to yield 14.5 g. of sirup which crystallized on standing. The identity of the regenerated product with the original anhydroxylitol was confirmed by the preparation of a tribenzoate, m. p. 79–80° giving no melting point depression when admixed with anhydroxylitol tribenzoate. Periodate oxidations, as described later, of the regenerated product and of the original anhydroxylitol gave the same results.

Monoanhydroxylitol Tribenzoate.—A mixture of 4.0 g. (0.03 mole) of anhydroxylitol, 17.0 g. (0.12 mole) of benzoyl chloride and 50 ml. of anhydrous pyridine was kept at room temperature for two days. The reaction mixture was taken up in chloroform, washed with dilute hydrochloric acid, saturated sodium bicarbonate solution and finally with water. Removal of solvent *in vacuo* yielded the ester as a sirup which was crystallized from 100 ml. of ethanol to yield 8.5 g. (63%) of the tribenzoate, m. p. 79–80°. *Anal.* Calcd. for C₂₅H₂₂O₇: C, 69.94; H, 4.97. Found: C, 69.9; H, 5.09.

Trityl Anhydroxylitol Diacetate.—A solution of 3.4 g. (0.025 mole) of anhydroxylitol and 7.25 g. (0.026 mole) of triphenylmethyl chloride in 20 ml. of anhydrous pyridine was heated under anhydrous conditions for two hours in a water-bath at 70–75° and then allowed to stand overnight at room temperature. Fifteen grams of acetic anhydride was added and the solution was allowed to stand for three days. The reaction mixture was poured into 500 g. of chopped ice and the solid precipitate (11 g.) was separated by filtration, dissolved in 300 ml. of benzene and washed four times with 100-ml. portions of water. Removal of solvent *in vacuo* resulted in a sirup which crystallized on trituration with 100 ml. of 95% ethanol to yield 7.0 g. (60%) of trityl anhydroxylitol diacetate which after three crystallizations from 10 parts of ethanol melted at 134–135°.

Anal. Calcd. for C₅H₇O₄(CH₃CO)₂C(C₆H₅)₃: C, 73.02; H, 6.13; CH₃CO, 18.69. Found: C, 72.9; H, 6.12; CH₃CO, 18.6 (saponification).

Oxidation of Anhydroxylitol with Sodium Metaperiodate.—To a solution of 0.6472 g. (4.825 millimoles) of anhydroxylitol (regenerated from the tricarbanilate) there was added 10 ml. of 0.5316 molar sodium meta-

(6) Bell, Carr and Krantz, *J. Phys. Chem.*, **44**, 862 (1940). Soltzberg, Goepf and Freudenberg, Abstract of paper, 105th meeting, American Chemical Society, Detroit, Michigan, April, 1943.

(7) Resinous Products and Chemical Co., Washington Square, Philadelphia, Pennsylvania.

(8) J. R. Matchett and J. Levine, *Ind. Eng. Chem., Anal. Ed.*, **15**, 296 (1943).

(9) Wolfrom and Pletcher, *THIS JOURNAL*, **62**, 1151 (1940).

(10) Salmon and Powell, *ibid.*, **61**, 2807 (1939).

periodate (5.316 millimoles) and the volume adjusted to 100 ml. Analyses of 10-ml. aliquots at the expiration of eight, twenty-four, thirty-two and forty-eight hours showed that 0.92, 1.03, 1.02, and 1.03 equivalents of oxidant had been consumed, respectively. Titration of aliquot samples with 0.02 *N* sodium hydroxide to methyl red showed no formic acid. No formaldehyde could be detected with a 0.4% dimethyldihydroresorcinol solution according to the procedure of Yoe and Reed.¹¹ Oxidation of a sample of the original anhydroxylitol with sodium metaperiodate gave similar results, 1.06 equivalents of oxidant being consumed after twenty-four hours.

Oxidation of Anhydroxylitol with Periodic Acid.—To 4.224 g. (0.03149 mole) of anhydroxylitol in 50 ml. of water was added 40 ml. of 0.872 molar periodic acid (0.0349 mole) and the solution was diluted exactly to 250 ml. with water. After thirty-six hours, titration of an aliquot portion for excess periodic acid indicated the consumption of 0.96 equivalent of oxidant. The remainder of the solution was neutralized with hot strontium hydroxide solution to a phenolphthalein end-point. The dialdehyde was obtained as a colorless sirup and was oxidized with bromine water in the presence of strontium carbonate according to the procedure of Jackson and Hudson.¹² After removal of excess bromine by aeration, bromide ion with silver carbonate, silver ion with hydrogen sulfide and hydrogen sulfide by aeration, the solution was concentrated *in vacuo* to about 15 ml. After standing at 0° for several weeks, the solution partly crystallized to yield 2.1 g. of strontium salt. On trituration with 50 ml. of methanol, the mother liquor yielded an additional 4.35 g. The salt was recrystallized twice from 10-ml. portions of water by the addi-

tion of 10 ml. of methanol and for analysis it was dried to constant weight at 112° *in vacuo*. The salt had the expected composition and is named strontium D,L-hydroxymethylidiglycolate. *Anal.* of anhydrous salt: Calcd. for SrC₆H₈O₆: C, 24.05; H, 2.42; Sr, 35.09. Found: C, 24.1; H, 2.35; Sr, 35.2. Analyses for water on the air-dried or humidified salt gave variable results indicating that a pure distinct hydrate is not easily formed which is in marked contrast to the strontium D-hydroxymethylidiglycolate tetrahydrate obtained by Richtmyer and Hudson¹³ from the oxidation of styracitol or polygalitol.

Acknowledgment.—The authors are indebted to Mr. Lawrence White for performing the micro analyses.

Summary

Xylitol has been dehydrated with benzenesulfonic acid or sulfuric acid to yield a mixture of dehydration products from which a pure anhydroxylitol has been isolated in crystalline form.

Anhydroxylitol has been characterized by the preparation of three crystalline derivatives, the tribenzoate, tricarbamate, and the monotrityl diacetate.

By oxidation with periodic acid and sodium metaperiodate, anhydroxylitol has been shown to contain a 1,4 oxygen ring and is designated as 1,4-anhydro-D,L-xylitol.

(1) Yoe and Reed, *Ind. Eng. Chem., Anal. Ed.*, **13**, 238 (1941).

(2) Jackson and Hudson, *THIS JOURNAL*, **59**, 999 (1937).

(13) Richtmyer and Hudson, *ibid.*, **65**, 64 (1943).

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The Preparation and Properties of Some Chloromethylchlorosilanes

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The methylchlorosilanes, described by Gilliam, Liebhafsky and Winslow¹ and Gilliam and Sauer,² have been shown by Gilliam³ to undergo both photochemical chlorination at room temperature and vapor phase chlorination at elevated temperatures in the presence of copper gauze to form chloromethylchlorosilane mixtures. The lower chlorination products of trimethylchlorosilane and dimethyldichlorosilane have now been isolated. Tetramethyl-1,3-bis-(chloromethyl)-disiloxane and pentamethylchloromethylidisiloxane have been prepared, respectively, by the hydroly-

sis of dimethylchloromethylchlorosilane and by the cohydrolysis of this compound with trimethylchlorosilane. The new compounds and their boiling points are listed in Table I.

From the relative yields of the various chlorination products it is apparent that a chloromethyl group is chlorinated in preference to an unsubstituted methyl group. This effect appears to be considerably more marked in the case of trimethylchlorosilane than in the analogous case of *t*-butyl chloride studied by Rogers and Nelson.⁴

Gilliam isolated Cl₃CSiCl₃ and found that on treatment with water, both the Si-Cl and Si-C bonds were hydrolyzed to produce silica, chloroform and hydrochloric acid. It has now been found that chloromethylchlorosilanes containing less than three chlorines in any methyl group are stable toward Si-C fission by acid catalyzed hydrolysis. With alkaline catalysts, however, even monochloromethyl groups undergo Si-C fission with the formation of methyl chloride, the ease of the reaction increasing with the degree of chlorination of the methyl groups. Use has been made of this reaction for the proof of configuration of several of the polychlorinated di- and tri-methyl-

TABLE I

	Compound	B. p., °C.
I	(CH ₃) ₂ (CH ₂ Cl)SiCl	115
II	(CH ₃) ₂ (CHCl ₂)SiCl	149
III	(CH ₃)(CH ₂ Cl) ₂ SiCl	172
IV	(CH ₃)(CH ₂ Cl)SiCl ₂	122
V	(CH ₃)(CHCl ₂)SiCl ₂	107 (225 mm.)
VI	(CH ₃)(CCl ₃)SiCl ₂	109 (150 mm.)
VII	[(CH ₃) ₂ (CH ₂ Cl)Si] ₂ O	205
VIII	(CH ₃) ₃ SiOSi(CH ₃) ₂ CH ₂ Cl	152

(1) W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, *THIS JOURNAL*, **65**, 801 (1941).

(2) W. F. Gilliam and R. O. Sauer, *ibid.*, **66**, 1793 (1944).

(3) Private communication.

(4) A. O. Rogers and R. E. Nelson, *THIS JOURNAL*, **58**, 1027 (1936).