carbonate, dried over magnesium sulfate and distilled to afford 15.5 g. (88%) of *cis*-3-methylcyclohexanemethanol (V), b.p. 90° (13.5 mm.), n^{21}D 1.4588. Mousseron and Granger[10] report for an optically active sample of V, b.p. 95° (25 mm.), n^{25}D 1.4557.

The **α-naphthylurethan**, prepared in the usual manner, crystallized from ligroin in fine needles, m.p. 80.5–81.7°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.95; H, 7.89; N, 4.68.

The **3,5-dinitrobenzoate**, prepared in the usual manner, crystallized from ethanol in large needles, m.p. 81.5–82.7°.

Anal. Calcd. for $C_{15}H_{18}N_2O_6$: C, 55.89; H, 5.63; N, 8.70. Found: C, 55.92; H, 5.80; N, 8.60.

Tosylate of *cis*-3-Methylcyclohexanemethanol (VI).—To an ice-cold solution of 13.7 g. of V in 50 ml. of pyridine was added 22.4 g. of *p*-toluenesulfonyl chloride dissolved in 22 ml. of pyridine. After the mildly exothermic reaction subsided, the mixture was warmed to 40° for one-half hour. The mixture was then poured into a mixture of 200 ml. of 6 *N* sulfuric acid and ice. The liberated oil was extracted with three 70-ml. portions of chloroform. The combined chloroform extracts were washed with dilute sulfuric acid and concentrated under reduced pressure to afford 30 g. (98%) of crude, clear oily tosylate. The tosylate was not purified further, but was reduced directly.

***cis*-1,3-Dimethylcyclohexane (VII).**—In a 500-ml. flask equipped with stirrer, reflux condenser and dropping funnel there were placed 275 ml. of anhydrous *n*-propyl ether and 11.75 g. of lithium aluminum hydride. After heating briefly to dissolve most of the lithium aluminum hydride, a solution of VI in 50 ml. of anhydrous *n*-propyl ether was added with stirring over a period of 40 minutes, maintaining the temperature at 70–75°. The mixture was stirred and heated at 70–75° for 24 hours. After cooling, excess lithium aluminum hydride was decomposed by the dropwise addition of water, followed by excess dilute sulfuric acid to dissolve the inorganic hydroxides. The *n*-propyl ether layer was separated, washed with 1 *N* sodium carbonate and dried over magnesium sulfate. Distillation through a 2-foot modified Podbielniak column afforded 3.79 g. (32% from V) of *cis*-1,3-dimethylcyclohexane, b.p. 119.8–120.3°, n^{25}D 1.4206, d^{25}_4 0.7629. During the distillation there was no indication of a higher boiling fraction. The reported properties[16] for the *cis*-1,3-dimethylcyclohexane are b.p. 120.09°, n^{25}D 1.42063, d^{25}_4 0.76196, whereas the following properties are reported for *trans*-1,3-dimethylcyclohexane; b.p. 124.45°, n^{25}D 1.4284, d^{25}_4 0.7806.

[16] A. F. Forziati, A. R. Glasgow, C. B. Willingham and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 129 (1946).

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1-Desoxy-D-xylitol and Some of Its Derivatives[1]

BY EMMANUEL ZISSIS AND NELSON K. RICHTMYER

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Sirupy 1-desoxy-D-xylitol, obtained by the reductive desulfurization of D-xylose diethyl mercaptal, has been characterized through its crystalline tetraacetyl, dibenzylidene and dimethylene derivatives. 1-Desoxy-2,4:3,5-dimethylene-D-xylitol is the enantiomorph of a compound prepared, in a different manner, by Ness, Hann and Hudson and reported in an accompanying paper. 1-Desoxy-2,4-methylene-D-xylitol, 1-desoxy-2,4-methylene-3,5-anhydro-D-xylitol, and other derivatives of 1-desoxy-D-xylitol have also been described.

In continuing our studies on the preparation and reactions of various ω-desoxy sugar alcohols,[1] we have desulfurized D-xylose diethyl mercaptal with Raney nickel and obtained 1-desoxy-D-xylitol (synonym, 5-desoxy-L-xylitol) as a thick, colorless sirup. The racemic form, 1-desoxy-D,L-xylitol, has been reported earlier from this Laboratory by Hann, Ness and Hudson,[2] and it also was a sirup; its synthesis from xylitol (a *meso* form) through 2,3,4,5-diisopropylidene-D,L-xylitol[3] could have produced only the racemic modification, whereas our reactions always involved optically active intermediates and produced the desired D-form. The new 1-desoxy-D-xylitol has been characterized through its crystalline tetraacetyl, dibenzylidene and dimethylene derivatives. Our 1-desoxy-2,3,-4,5-dibenzylidene-D-xylitol is recognized as one component of the racemic 1-desoxy-2,3,4,5-dibenzylidene-D,L-xylitol whose preparation from the long-known dibenzylidenexylitol is described in the accompanying paper from this Laboratory by Ness, Hann and Hudson.[4] Furthermore, our dimethylene derivative must be 1-desoxy-2,4:3,5-dimethylene-D-xylitol because it proved to be the enantiomorph of the 1-desoxy-2,4:3,5-dimethylene-L-xylitol described in the accompanying paper.[4] The location of the methylene groups in the latter compound follows from the earlier proof of structure of the 2,4:3,5-dimethylene-L-xylitol[5] from which it was derived. This pair of enantiomorphs composes the previously described racemic 1-desoxy-2,4:3,5-dimethylene-D,L-xylitol.[6] A comparison of melting points of these and other derivatives of 1-desoxy-D-xylitol and 1-desoxy-D,L-xylitol, together with their mixed melting points, is given in Table I.

Acetolysis of 1-desoxy-2,4:3,5-dimethylene-D-xylitol to 1-desoxy-2,4-methylene-3-acetoxymethyl-5-acetyl-D-xylitol[7] and subsequent saponification has furnished 1-desoxy-2,4-methylene-D-xylitol. The racemic 1-desoxy-2,4-methylene-D,L-xylitol was known from an earlier publication.[8] Tosylation of the new compound could be controlled to yield either the ditosyl or a monotosyl derivative. The ditosyl derivative appeared to be quite resistant to the exchange reaction with sodium iodide under the

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[1] Presented in part before the Division of Sugar Chemistry at the Atlantic City Meeting of the American Chemical Society, September 15, 1952. For the preceding paper in this series, see E. Zissis and N. K. Richtmyer, THIS JOURNAL, **74**, 4373 (1952).

[2] R. M. Hann, A. T. Ness and C. S. Hudson, *ibid.*, **66**, 73 (1944).

[3] R. S. Tipson and L. H. Cretcher, *J. Org. Chem.*, **8**, 95 (1943).

[4] A. T. Ness, R. M. Hann and C. S. Hudson, THIS JOURNAL, **75**, 132 (1953).

[5] A. T. Ness, R. M. Hann and C. S. Hudson, *ibid.*, **66**, 665 (1944).

[6] R. M. Hann, A. T. Ness and C. S. Hudson, *ibid.*, **66**, 670 (1944).

[7] Allocation of the acetoxymethyl group to the secondary hydroxyl is based on the studies of the acetolysis of trimethylene-D-mannitol [A. T. Ness, R. M. Hann and C. S. Hudson, *ibid.*, **65**, 2215 (1943)] and dimethylene-L-xylitol (ref. 5).

[8] R. M. Hann, N. K. Richtmyer, H. W. Diehl and C. S. Hudson, *ibid.*, **72**, 561 (1950).

TABLE I

MELTING POINTS OF DERIVATIVES OF 1-DESOXY-D-XYLITOL AND 1-DESOXY-D,L-XYLITOL, °C.

Derivative	1-Desoxy-D-xylitol	1-Desoxy-D,L-xylitol	1:1 Mixture of D- and D,L-forms
2,3,4,5-Dibenzylidene	175–176	173–174[a]	174–175
2,4:3,5-Dimethylene	154–155[b]	155–156[c]	143–153
2,4-Methylene	70–72	52–53[d]	45–55
2,4-Methylene-3,5-benzylidene	165–167	140–141[d]	139–155
2,4-Methylene-3,5-ditosyl	99–100	112–113[d]	93–103
2,4-Methylene-5-tosyl	62–68[e]	145–146[d]	63–145
2,4-Methylene-3,5-anhydro	84–85	64–65[d]	63–81

[a] A. T. Ness, R. M. Hann and C. S. Hudson, ref. 4. [b] For a comparison of the D- and L-forms, see the Experimental part. [c] R. M. Hann, A. T. Ness and C. S. Hudson, ref. 6. [d] R. M. Hann, N. K. Richtmyer, H. W. Diehl and C. S. Hudson, ref. 8. [e] A hydrated form; see Experimental part.

usual conditions and attempts to force the reaction by longer heating or at higher temperatures resulted principally in deep-seated destruction. The crystalline monotosyl derivative was judged to be the 5-tosyl derivative because its acetate, when refluxed with sodium iodide in methyl ethyl ketone for 15 hours, was converted in part to a low-melting iodo compound with the expected composition.

The 1-desoxy-2,4-methylene-5-tosyl-D-xylitol reacted readily in acetone solution with dilute alkali, eliminating a molecule of *p*-toluenesulfonic acid and forming an anhydride, namely, 1-desoxy-2,4-methylene-3,5-anhydro-D-xylitol. In the D,L-xylitol series,[8] 1-tosyl-2,4-methylene-D,L-xylitol (of established structure) had been converted similarly to an anhydride, and the structure of the latter proved by transformation of its free CH_2OH group to a CH_3 group. The resulting compound, 1-desoxy-2,4-methylene-3,5-anhydro-D,L-xylitol, like the new D-form, was appreciably volatile and had a faint, aromatic odor, as we have since determined.

Experimental

1-Desoxy-D-xylitol.—To obtain a starting material for 1-desoxy-D-xylitol, it was necessary first to prepare **D-xylose diethyl mercaptal.** Wolfrom, Newlin and Stahly[9] had synthesized the latter substance using concentrated hydrochloric acid as the condensing agent. In an alternative procedure, we substituted anhydrous zinc chloride. Thus, a mixture of 25 g. of finely powdered D-xylose, 25 g. of powdered, freshly fused zinc chloride, and 60 ml. of technical ethyl mercaptan was shaken mechanically overnight. The supernatant excess mercaptan was decanted, and the thick sirupy residue, still containing pieces of solid zinc chloride, was stirred with 400 ml. of ice and water until solution was complete. The mercaptan odor in the solution was removed by bubbling a slow stream of air through it for 2 or 3 days. The filtered, nearly colorless solution had a rotation of about $[\alpha]^{20}\mathrm{D}$ −24° (calculated as the mercaptal) as compared to the value $[\alpha]^{25}\mathrm{D}$ −30.8° in water reported for the pure mercaptal.[9] Isolation of the D-xylose diethyl mercaptal, which is very readily soluble in water, was accomplished through removal of the zinc chloride with Amberlite IR-120 and Duolite A-4 ion-exchange columns, and concentration of the solution *in vacuo* to a thick sirup. Solution of this sirup in a small amount of warm absolute ethanol, followed by crystallization and filtration at −5°, then gave about a 65% yield of the mercaptal. Occasionally the product was contaminated with D-xylose that had escaped mercaptal formation; therefore, a recrystallization was desirable, with absolute ethanol being used to dissolve the mercaptal and leave behind any of the difficulty soluble D-xylose.

The reductive desulfurization of D-xylose diethyl mercaptal with Raney nickel in the usual manner produced 1-desoxy-D-xylitol as a sirup that could be purified through its crystalline tetraacetate described below.

1-Desoxy-2,3,4,5-tetraacetyl-D-xylitol.—The acetylation of 12.6 g. of crude 1-desoxy-D-xylitol sirup with acetic anhydride and fused sodium acetate by heating for 2 hours on the steam-bath yielded 19 g. (67%) of solid product. After 2 recrystallizations from a mixture of chloroform and pentane, the flattened, nearly rectangular prisms of 1-desoxy-2,3,4,5-tetraacetyl-D-xylitol melted at 62–63° and showed $[\alpha]^{20}\mathrm{D}$ +10.4° in chloroform (*c* 1.0). Deacetylation of the purified substance has so far failed to produce crystalline 1-desoxy-D-xylitol.

Anal. Calcd. for $C_{13}H_{20}O_8$: C, 51.31; H, 6.63; CH_3CO, 56.58. Found: C, 51,20; H, 6.57; CH_3CO, 56.42.

1-Desoxy-2,3,4,5-dibenzylidene-D-xylitol.—A solution of 0.5 g. of 1-desoxy-D-xylitol (regenerated from its tetraacetate) in 2 ml. of concentrated hydrochloric acid was cooled in an ice-bath and to it was added 1.5 ml. of benzaldehyde. The acetal, which crystallized readily, was allowed to stand for 1 hour at 5°, then filtered and washed successively with cold 5% aqueous sodium hydroxide, water and ether. The yield was 1.2 g. of dried product (quantitative). From benzene the dibenzylidene derivative separated as silky needles, and after 2 recrystallizations melted at 175–176° and showed $[\alpha]^{20}\mathrm{D}$ −34.5° in chloroform (*c* 0.4).

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.00; H, 6.72.

1-Desoxy-2,4:3,5-dimethylene-D-xylitol.—A solution of 6.3 g. of 1-desoxy-D-xylitol (regenerated from its tetraacetate) in 12 ml. of 37% formaldehyde and 12 ml. of concentrated hydrochloric acid was heated in a stoppered flask for 2 hours at 50°, and the mixture allowed to concentrate to dryness in an evacuated desiccator over solid potassium hydroxide. The residue, on crystallization from chloroform by the addition of pentane, yielded a total of 5.6 g. (76%) of product melting at 153–155°. After 1 recrystallization in the same manner, the fine needles of 1-desoxy-2,4:3,5-dimethylene-D-xylitol melted at 154–155° and showed $[\alpha]^{20}\mathrm{D}$ +16.5° in chloroform (*c* 1) and $[\alpha]^{20}\mathrm{D}$ +33.3° in water (*c* 1). The antipodal 1-desoxy-2,4:3,5-dimethylene-L-xylitol[4] was reported to melt at 154–155° and show $[\alpha]^{20}\mathrm{D}$ −33.1° in water (*c* 0.8).

The condensation of formaldehyde with crude, sirupy 1-desoxy-D-xylitol that had not been purified through its tetraacetate afforded the same dimethylene derivative but only in about 30% yield.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.57; H, 7.55.

When equal amounts (100 ± 0.2 mg.) of the new D-form and the original L-form[4] were mixed intimately, the m.p. was depressed to 149–154°. However, when the same mixture was recrystallized from ethanol, it melted quite sharply at 155–156°. A sample of the original D,L-form[6] melted, according to our thermometer, at 156–157° and a mixture with the new, synthetic D,L-form also melted at 156–157°.

1-Desoxy-2,4-methylene-3-acetoxymethyl-5-acetyl-D-xylitol.[7]—Two grams of 1-desoxy-2,4:3,5-dimethylene-D-xylitol was shaken 15 minutes in an ice-bath with 12 ml. of a solution prepared by adding 2 ml. of concentrated sulfuric acid to a cold mixture of 70 ml. of acetic anhydride and 30 ml. of glacial acetic acid. The clear reaction mixture was poured on cracked ice, and the resulting solution was neutralized with solid sodium bicarbonate and then extracted with chloroform. The chloroform solution was washed successively with aqueous bicarbonate and water, dried and concentrated *in vacuo* to a crystalline residue. From chloroform-pentane solution there was obtained 1.8 g. (55%) of acetolysis product; 2 recrystallizations produced silky needles with m.p. 110–111° and $[\alpha]^{20}\mathrm{D}$ −18.0° in chloroform (*c* 0.7).

Anal. Calcd. for $C_{11}H_{18}O_7$: C, 50.38; H, 6.92; CH_3CO, 32.8. Found: C, 50.48; H, 7.16; CH_3CO, 32.9.

1-Desoxy-2,4-methylene-D-xylitol.—Removal of the acetyl and acetoxymethyl groups from the preceding compound was effected by dissolving 4 g. of it in 100 ml. of water, adding 46 ml. of *N* sodium hydroxide, and allowing the solution

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(9) M. L. Wolfrom, M. R. Newlin and E. E. Stahly, THIS JOURNAL, 53, 4379 (1931).

to stand 5 hours at 20°. Neutralization of the excess alkali required 11.2 ml. of *N* sulfuric acid, indicating the consumption of 2.3 molar equivalents of alkali. The neutral solution was concentrated *in vacuo* to a residue that was extracted with chloroform; the latter solution was concentrated, the residue taken up in water and deionized with a suitable pair of ion-exchange columns; and the aqueous solution was finally concentrated *in vacuo* to a sirup. Digestion of this sirup with ether and chilling the ethereal solution overnight in the refrigerator yielded 1.4 g. (62%) of elongated flat prisms. After 1 recrystallization from ether the 1-desoxy-2,4-methylene-D-xylitol melted at 70–72° and showed $[\alpha]^{20}\text{D}$ +5.9° in chloroform (*c* 0.5).

Anal. Calcd. for $C_6H_{12}O_4$: C, 48.64; H, 8.17. Found: C, 48.89; H, 7.91.

1-Desoxy-2,4-methylene-3,5-benzylidene-D-xylitol.—The condensation of 0.5 g. of 1-desoxy-2,4-methylene-D-xylitol with benzaldehyde in the presence of hydrochloric acid in the usual way yielded 0.55 g. (69%) of the mixed acetal. Recrystallization, twice from ethanol and once from chloroform–pentane, produced fine needles with $[\alpha]^{20}\text{D}$ +26.3° in chloroform (*c* 0.9) and m.p. 160–162°. Three months later the m.p. was found to be 165–167°, a value that has remained constant for 7 additional months.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.07; H, 6.66.

1-Desoxy-2,4-methylene-3,5-ditosyl-D-xylitol.—The reaction overnight of 2 g. of 1-desoxy-2,4-methylene-D-xylitol with 8 g. of *p*-toluenesulfonyl chloride in 10 ml. of dry pyridine gave 6.2 g. (quantitative) of solid when the reaction mixture was poured on cracked ice. After 2 recrystallizations from ethanol the clusters of long needles melted at 99–100° and showed $[\alpha]^{20}\text{D}$ −18.7° in chloroform (*c* 1).

Anal. Calcd. for $C_{20}H_{24}O_8S_2$: C, 52.62; H, 5.30; S, 14.05. Found: C, 52.62; H, 5.29; S, 13.97.

The infrared absorption spectra (in chloroform solution) of the new D-form and the original D,L-form[8] were practically identical, and furnished additional evidence that the two substances are optical and not structural isomers.

Attempts to obtain a successful replacement of the 5-tosyloxy group by an iodine atom were disappointing. Thus, when the ditosyl compound was refluxed with an equal weight of sodium iodide in boiling acetone for 200 hours, 85% of the starting product was recovered unchanged. Boiling for 124 hours in methyl ethyl ketone produced 1 equivalent of sodium *p*-toluenesulfonate, but the dark red mother liquor proved to contain at least 30% of unchanged ditosyl compound. The reaction in acetone in a sealed tube for 2.5 hours at 100° yielded about 0.65 mole of sodium tosylate, yet nearly 75% of the starting product was recovered. Even the addition of an equal weight of sodium bicarbonate, a method that proved effective in an earlier case,[4] failed to stabilize the expected iodo compound, and after heating for 5 hours in acetonylacetone at 120° only a black tar could be obtained. Finally, a mixture of 1 g. of the ditosyl compound, 1 g. of sodium iodide and 1 g. of sodium bicarbonate in 50 ml. of methyl ethyl ketone was refluxed for 287 hours. The insoluble sodium bicarbonate and sodium *p*-toluenesulfonate were removed by filtration, and the filtrate was concentrated to a small volume. The addition of water precipitated a small amount of tan-colored crystalline material weighing 0.1 g. The filtrate was concentrated to a dark, brownish residue that was readily soluble in a few drops of water; this indicated that most of the original ditosyl compound had undergone deep-seated destruction with loss of both tosyl groups. The small amount of crystalline material was recrystallized once from 95% ethanol and twice from 50% ethanol. The fine, colorless needles (20 mg.) melted at 123–125° and the compound was concluded to be **1,5-didesoxy-2,4-methylene-3-tosyl-5-iodo-D-xylitol.**

Anal. Calcd. for $C_{13}H_{17}IO_5S$: C, 37.87; H, 4.16; I, 30.8. Found: C, 38.04; H, 4.39; I, 30.7.

1-Desoxy-2,4-methylene-5-tosyl-D-xylitol.—To a mechanically stirred solution of 2.781 g. of 1-desoxy-2,4-methylene-D-xylitol in 20 ml. of dry pyridine at 0° was added dropwise a solution of 3.578 g. (1.000 molar equivalent) of freshly recrystallized *p*-toluenesulfonyl chloride in 20 ml. of dry pyridine. The mixture was stirred an additional half-hour at 0°, left 2 hours at room temperature, and then poured on cracked ice. Overnight in the refrigerator the solution deposited 1.2 g. (14%) of the ditosyl compound described above. The filtrate from the ditosyl compound was concentrated *in vacuo* and the residue taken up in chloroform; this solution was dried with anhydrous sodium sulfate and again concentrated to a mobile sirup. A small amount of the sirup, covered with a mixture of ether and pentane and kept overnight on Dry Ice, crystallized when rubbed. The remainder of the sirup was dissolved in ethanol and diluted with water to incipient cloudiness. When seeded and cooled overnight in the refrigerator, the solution deposited 3 g. of the new monotosyl compound. It was recrystallized several times from ether–pentane, separating overnight as clusters of prisms that melted at 62–68°. From chloroform–pentane only a negligible amount of crystals separated overnight, but upon the addition of a few drops of water crystallization proceeded readily. These observations, together with the analyses, indicate that the substance contains one-third of a molecule of water. The value $[\alpha]^{20}\text{D}$ −2.1° in chloroform (*c* 0.85) was found for the hydrated monotosyl compound.

Anal. Calcd. for $C_{13}H_{18}O_6S{\cdot}{}^1/_3H_2O$: C, 50.64; H, 6.10; S, 10.40; H_2O, 1.95. Found: C, 50.58; H, 6.09; S, 10.44; H_2O (dried 2 hours at 57° *in vacuo*), 1.77. Calcd. for $C_{13}H_{18}O_6S$: C, 51.64; H, 6.00. Found (on dried sample): C, 51.49; H, 5.84.

1-Desoxy-2,4-methylene-3,5-anhydro-D-xylitol.—A solution of 2.4 g. of 1-desoxy-2,4-methylene-5-tosyl-D-xylitol in a mixture of 300 ml. of acetone, 20 ml. of water and 9.5 ml. of *N* sodium hydroxide was refluxed 1 hour. For neutralization, 1.75 ml. of *N* sulfuric acid was required, indicating the consumption of 1.00 molar equivalent of alkali. The solution was concentrated *in vacuo*, the residue extracted with ether, and the extract, on concentration and chilling, deposited 0.45 g. (44%) of the expected anhydro compound. The product was recrystallized from pentane, forming flat, elongated prisms melting at 84–85° and showing $[\alpha]^{20}\text{D}$ +28.6° in water (*c* 0.5). The anhydro compound is appreciably volatile in the air at room temperature and has a slight, camphor-like odor.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.36; H, 7.66.

1-Desoxy-2,4-methylene-3-acetyl-5-tosyl-D-xylitol.—The acetylation of 0.6 g. of 1-desoxy-2,4-methylene-5-tosyl-D-xylitol with acetic anhydride and pyridine resulted in a practically quantitative yield of the 3-acetyl derivative. The latter was recrystallized once from 95% ethanol and once from 50% ethanol; the shiny needles melted at 101–102° and showed $[\alpha]^{20}\text{D}$ −5.3° in chloroform (*c* 1).

Anal. Calcd. for $C_{15}H_{20}O_7S$: C, 52.31; H, 5.85; S, 9.31; CH_3CO, 12.5. Found: C, 52.51; H, 5.83; S, 9.07; CH_3CO, 12.5.

1,5-Didesoxy-2,4-methylene-3-acetyl-5-iodo-D-xylitol.—A mixture of 0.82 g. of 1-desoxy-2,4-methylene-3-acetyl-5-tosyl-D-xylitol and 0.85 g. of sodium iodide in 15 ml. of methyl ethyl ketone was refluxed for 15 hours. The first 5 hours produced 0.17 g. of crystalline sodium tosylate, the second 0.11 g., and the third 0.05 g., for a total of 0.33 g. (71%). The filtrate from the third crop was concentrated to a small volume, diluted with water, and 0.2 g. (24%) of starting product recovered. The mother liquor was extracted with chloroform and the extract concentrated to a sirup that crystallized when its aqueous ethanolic solution was left overnight in the refrigerator. The product (0.2 g.) was recrystallized twice from aqueous ethanol, forming clusters of needles melting at 51–52°.

Anal. Calcd. for $C_8H_{13}IO_4$: C, 32.02; H, 4.37; I, 42.3. Found: C, 32.15; H, 4.29; I, 42.9.

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