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THE SYNTHESIS OF 3,4-DIDEOXYHEX-3-ENITOLS

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ABSTRACT

Syntheses of (*E*)-3,4-dideoxy-*erythro*-, (*Z*)-3,4-dideoxy-D-*threo*- and (*E*)-3,4-dideoxy-D-*threo*-hex-3-enitols are described. The action of potassium selenocyanate on 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-di-*p*-toluenesulfonate has been re-examined. Epoxidation of (E)-3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-D-*threo*-hex-3-enitol affords 3,4-anhydro-1,2:5,6-di-*O*-isopropylidene-D-mannitol and -D-iditol in the approximate proportions of 3:1. The configurations of the two epoxides were assigned on the basis of the reaction of the latter compound with sodium methoxide to give 1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-D-altritol.

INTRODUCTION

3,4-Dideoxyhex-3-enitols or their *O*-glycosyl derivatives have been isolated from certain blood-group substances by the action of sodium hydroxide–sodium borohydride mixtures[1]. In connection with studies on the base-catalyzed degradations of carbohydrates[2,3] we discuss syntheses of three of the stereoisomers.

DISCUSSION

1,2:5,6-Di-*O*-isopropylidene derivatives (**1** and **2**) of (*E*)-3,4-dideoxy-D-*threo*- (**3**) and (*Z*)-3,4-dideoxy-D-*threo*- (**4**) hex-3-enitols are most conveniently prepared from the corresponding D-mannitol (**5**) and D-altritol (**6**) derivatives by the stereospecific Corey–Winter procedure[4] through treatment of the cyclic 3,4-thionocarbonates with trimethyl phosphite, as reported by Haines[5]. Similarly 1,2:5,6-di-*O*-isopropylidene-D-glucitol[6] (**7**) was converted via the thionocarbonate (**8**) into the known (*E*)-3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-*erythro*-hex-3-enitol[7] (**9**). As described by Anet[7] for the latter compound **9**, mild acid hydrolysis of the di-*O*-isopropylidene derivatives furnished the parent 3,4-dideoxyhex-3-enitols (**3**, **4**, and **10**).

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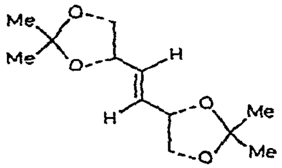
†Taken in part from the M.Sc. thesis of S. C. Tam, Trent University, 1973.



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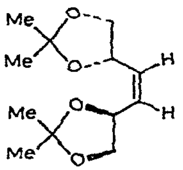

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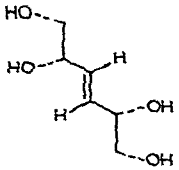

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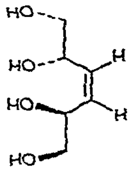

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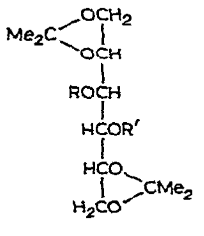

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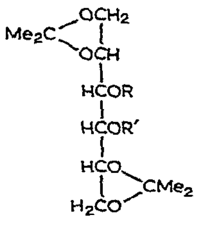
11 R=R'=Ts
19 R=Me,R'=H
20 R=Me R'=Ac



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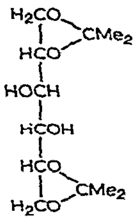
15 R=Me,R'=H
16 R=H,R'=Me
17 R=Me,R'=Ac
18 R=Ac,R'=Me



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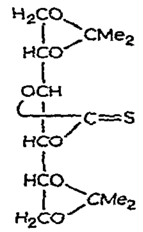

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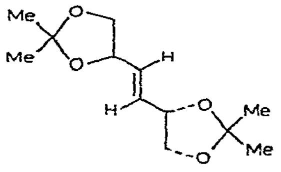
Van Es[8] has reported a synthesis of (*Z*)-3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-D-*threo*-hex-3-enitol (2) by heating the readily available 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-di-*p*-toluenesulfonate (11) with potassium selenocyanate in *N*,*N*-dimethylformamide. Although certain of the physical properties of the syrupy product were similar to those previously reported[5], unambiguous proof of structure was lacking. In our hands, however, this procedure resulted in the isolation, in low yield, of the crystalline (*E*)-D-*threo*-compound (1) and only traces of the (*Z*)-D-*threo* isomer (2) could be detected. The formation of the (*E*)-D-*threo* compound (1) in this reaction appears to follow the same stereochemical pathway as in its formation from the same D-mannitol derivative (11) in the Tipson–Cohen reaction[9], and presumably involves displacement of *p*-toluenesulfonate by the attacking nucleophile followed by *trans*-elimination[10]. On the other hand, the action of potassium selenocyanate on 3,4-anhydro-1,2:5,6-di-*O*-isopropylidene-D-altritol[11] (12) gave, as reported by Van Es[8], (*Z*)-3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-D-*threo*-hex-3-enitol (2), and no trace of the (*E*)-D-*threo* isomer (1) could be detected. In this case, presumably, epoxide opening is followed by *trans*-elimination.

In the course of synthesizing a reference sample of the (*Z*)-3,4-dideoxy-D-*threo*-hex-3-enitol derivative (2) by the stereospecific thionocarbonate method, 1,2:5,6-di-*O*-isopropylidene-D-altritol (6) was prepared by epoxidation of the (*E*)-3,4-dideoxy-D-*threo*-hex-3-enitol derivative (1) with *m*-chloroperoxybenzoic acid followed by reaction of the mixture of epoxides with potassium hydroxide. The epoxides formed in this reaction were separated by chromatography on silica gel to give syrupy epoxide A (13) and crystalline epoxide B (14) in the approximate proportions of 3:1. Both epoxides were opened by reaction with sodium methoxide to give single



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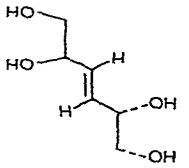

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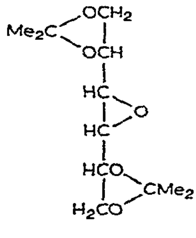

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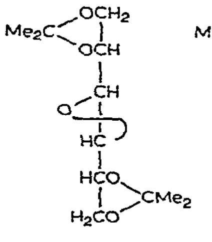

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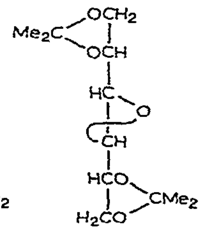

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products (**15** and **16**), and the derived *O*-acetyl-di-*O*-isopropylidene-*O*-methyl-D-altritols (**17** and **18**) were readily distinguishable by g.l.c. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-methyl-D-mannitol[12] (**19**) was converted into a mixture of 3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-D-mannitol (**20**) and the epimeric D-altritol derivative (**18**) by oxidation with methyl sulfoxide–acetic anhydride, followed by reduction with sodium borohydride and acetylation. The newly formed D-altritol derivative was readily distinguishable on g.l.c. from both the D-mannitol derivative (**20**) and the D-altritol derivative (**17**) formed from epoxide A (**13**), but was indistinguishable from the D-altritol derivative (**18**) formed from epoxide B (**14**). It follows that epoxides A and B are 3,4-anhydro-1,2:5,6-di-*O*-isopropylidene-D-mannitol (**13**) and -D-iditol (**14**), respectively. Inspection of molecular models indicated that reaction of (*E*)-3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-D-*threo*-hex-3-enitol (**1**) in the zig-zag conformation would thus lead to the preferential formation of the 3,4-anhydro-D-mannitol derivative (**13**).

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were measured with a Perkin–Elmer model 141 polarimeter at 20 ±2°. I.r. spectra were measured on a Unicam SP 200 spectrophotometer. N.m.r. spectra were recorded on a JEOL C-60HL spectrophotometer with tetramethylsilane or sodium 4,4-dimethyl-4-silapentanesulfonate as internal standards. Plates for t.l.c. were prepared with Kieselgel GF 254 (Merck) as adsorbent, and the dried plates were sprayed with 5% ethanolic sulfuric acid. Column chromatography was carried out on silica gel (Davison grade 950, 60–200 mesh). Unless otherwise stated, light petroleum refers to the fraction of b.p. 30–60°. Solutions were concentrated below 50° under diminished pressure.

Mass spectra were recorded on an A.E.I. MS-12 mass spectrometer, with an ionization potential of 70 eV. G.l.c. was performed with a Hewlett–Packard model 5750 chromatograph by using a column of dichlorodimethylsilane-treated Celite coated with 3% of silicone gum XE-60 (operating temperature 180°). For g.l.c.–mass spectrometry, a similar column was used in a Pye 104 chromatograph and attached to the mass spectrometer via a Watson–Biemann separator. The mass spectra were recorded at an inlet temperature of 200°, an ionization potential of 70 eV, and an ion-source temperature of ~150°.

*1,2:5,6-Di-*O*-isopropylidene-*D*-glucitol 3,4-thionocarbonate* (**8**). — Sodium hydroxide (5M, 15 ml) and carbon disulfide (15 ml) were stirred with 1,2:5,6-di-*O*-isopropylidene-D-glucitol[6] (**7**, 15 g) in 1,4-dioxane (75 ml) for 45 min, and the base neutralized with 5M acetic acid. Iodine solution (0.3M) was added until a slight excess of iodine remained on prolonged stirring. The solution was concentrated to a syrup, which was washed with water and dissolved in pyridine (20 ml). The solution was kept until deposition of sulfur was complete and concentrated to a crystalline mass, which was recrystallized from butyl ether to give the thionocarbonate **8** (5.5 g), m.p. 102–103°, $[\alpha]_D$ +23.3° (*c* 2.0, chloroform).

Anal. Calc. for $C_{13}H_{20}O_6S$: C, 51.31; H, 6.57; S, 10.52. Found: C, 51.13; H, 6.95; S, 10.38.

(E)*-3,4-Dideoxy-1,2:5,6-di-*O*-isopropylidene-*erythro*-hex-3-enitol* (**9**). — The thionocarbonate **8** (3.5 g) in trimethyl phosphite (53 ml, freshly distilled) was heated for 70 h under reflux in an atmosphere of nitrogen. Sodium hydroxide (6M) was added to the vigorously stirred solution until permanent alkalinity was attained. The mixture was extracted with chloroform (4 × 50 ml), and the combined extracts were washed with water, dried, and concentrated to a crystalline residue, which was triturated with light petroleum and recrystallized from ethanol to give compound **9** (1.45 g), m.p. 68–70° [lit.[7], m.p. 70–71°]. N.m.r. data ($CDCl_3$): τ 4.32 (2-proton sextet, $J_{3,4}$ 16.5 Hz, H-3 and H-4), 8.59, 8.61 (26-proton singlets, $2CMe_2$).

*The action of potassium selenocyanate on 1,2:5,6-di-*O*-isopropylidene-*D*-mannitol 3,4-di-*p*-toluenesulfonate* (**11**). — 1,2:5,6-Di-*O*-isopropylidene-D-mannitol 3,4-di-*p*-toluenesulfonate[13] (**11**, 1.12 g) and potassium selenocyanate (1.0 g) were heated for 4 h under reflux in *N,N*-dimethylformamide (10 ml). The cooled solution was diluted with water and extracted with chloroform, and the extract was washed with water, dried, and concentrated to a brown oil to which light petroleum was added. The solution was kept overnight in the cold, whereupon unchanged starting material (250 mg) was deposited, and concentration of the mother liquor furnished (*E*)-3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-D-*threo*-hex-3-enitol (**1**), which was recrystallized (yield, 115 mg) from light petroleum and had m.p. 77–78° and $[\alpha]_D$ +57.6° (*c* 0.34, chloroform) [lit.[9], m.p. 80–82°, $[\alpha]_D$ +57.5°]; n.m.r. data ($CDCl_3$): τ 4.32 (2-proton sextet, $J_{3,4}$ 16.5 Hz, H-3 and H-4), 8.58, 8.61 (26-proton singlets, $2CMe_2$). The n.m.r. spectrum was identical with that of a sample prepared by the Tipson–Cohen[9] procedure. Examination of the mother liquors by n.m.r. spectroscopy failed to reveal more than a trace of the (*Z*)-D-*threo* isomer. The reaction was performed on a small scale (with 20 mg of compound **11**) and aliquot portions were withdrawn at intervals and examined by g.l.c. Compounds **1** and **2** were well separated and the results indicated the formation of the (*E*)-compound (**1**) as the major product with only traces of the (*Z*) isomer (**2**).

*The action of potassium selenocyanate on 3,4-anhydro-1,2:5,6-di-*O*-isopropylidene* D-*altritol* (**12**). — The anhydride[11] **12** (2.53 g) and potassium selenocyanate (5.76 g) in 2-ethoxyethanol (25 ml) and water (30 ml) were heated for 6.5 h under reflux. The cooled solution was filtered, the filtrate was extracted with light petroleum and ether, and the combined extracts were washed with water, decolorized, dried, and concentrated to a syrup (1.6 g). The syrup was chromatographed on silica gel by elution with 4:1 light petroleum–ether to give (*Z*)-3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-D-*threo*-hex-3-enitol (**2**, 1.2 g), $[\alpha]_D$ −6.5° (*c* 1.8, chloroform), which was homogeneous on t.l.c. and g.l.c., and whose n.m.r. and i.r. spectra were identical with those of a sample prepared from 1,2:5,6-di-*O*-isopropylidene-D-altritol 3,4-thionocarbonate[5]. The n.m.r. spectrum showed a sextet at τ 4.41 ($J_{3,4}$ 11.3 Hz) which was clearly distinguishable from the corresponding signal in the spectrum of the (*E*) isomer (**1**).

*Hydrolysis of di-*O*-isopropylidene derivatives of 3,4-dideoxyhex-3-enitols.* — The di-*O*-isopropylidene compound **2** (1 g) was kept in 4:1 acetic acid–water for 22 h at room temperature. The solution was concentrated to a crystalline residue, which was recrystallized from ethanol–ethyl acetate to give (*Z*)-3,4-dideoxy-D-*threo*-hex-3-enitol (**4**, 469 mg), m.p. 72–74°, $[\alpha]_D$ +13.3° (*c* 0.18, water); n.m.r. data (D_2O): τ 4.37 (2-proton sextet, $J_{3,4}$ 11.3 Hz, H-3 and H-4).

Anal. Calc. for $C_6H_{12}O_4$: C, 48.64; H, 8.16. Found: C, 48.67; H, 7.97.

In a similar manner, hydrolysis of the di-*O*-isopropylidene derivative **1** (1 g) afforded (*E*)-3,4-dideoxy-D-*threo*-hex-3-enitol (**3**, 512 mg), m.p. 61–62°, $[\alpha]_D$ −13.3° (*c* 0.69, water) [lit.[9], m.p. 64–65°, $[\alpha]_D$ −13.8°]; n.m.r. data (D_2O): τ 4.16 (2-proton sextet, $J_{3,4}$ 16.5 Hz).

Likewise, hydrolysis of the di-*O*-isopropylidene derivative **9** (1 g) furnished (*E*)-3,4-dideoxy-*erythro*-hex-3-enitol (**10**), 466 mg, m.p. 114–115°, $[\alpha]_D$ 0° (*c* 0.72, water) [lit.[7], m.p. 114–114.5°]; n.m.r. data (D_2O): τ 4.16 (2-proton sextet $J_{3,4}$ 16.5 Hz, H-3 and H-4).

Epoxidation of (E)-*3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-*D-threo-*hex-3-enitol* (**1**). — The hex-3-enitol derivative **1** (4.7 g) in dichloromethane (37 ml) was treated with *m*-chloroperoxybenzoic acid (5 g) at room temperature and the reaction was monitored by g.l.c. After 92 h, starting material had completely disappeared, g.l.c. showed the formation of two components in the approximate ratio of 3:1, and g.l.c.–mass spectrometry established the structural similarity of the two compounds, whose mass spectra showed strong fragment ions at *m/e* 229 (corresponding to M − 15 for stereoisomeric epoxides). The reaction mixture was extracted with sodium hydrogen carbonate solution to remove *m*-chlorobenzoic acid and excess of peroxy acid, washed with water, dried, and concentrated to a syrup (4.17 g). The syrup was heated in 2M potassium hydroxide (100 ml) for 22 h on a boiling-water bath. The cooled solution was extracted with chloroform, and the extract was washed with water, dried, and concentrated to a crystalline residue, which was recrystallized from light petroleum to give 1,2:5,6-di-*O*-isopropylidene-D-altritol (**6**, 2.78 g), m.p. 63–64°, $[\alpha]_D$ +5.1° (*c* 2.2, chloroform) (lit.[14], m.p. 64.5–65.5°, $[\alpha]_D$ +5.2°).

A sample (2.5 g) of the afore-mentioned syrupy mixture of epoxides was repeatedly chromatographed on silica gel with 20:1 ether–cyclohexane as eluant to give epoxides A (1.2 g) and B (0.54 g). Epoxide A was a syrup, $[\alpha]_D$ +26.5° (*c* 1.0, chloroform); n.m.r. data ($CDCl_3$): τ 7.04 (2-proton multiplet, H-3 and H-4), 8.57, 8.67 (2 × 6-proton singlets, 2 × CMe_2).

Anal. Calc. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.03; H, 8.33. Epoxide B had m.p. 73–75°, $[\alpha]_D$ −3.4° (*c* 1.0, chloroform); n.m.r. data ($CDCl_3$): τ 6.97 (2-multiplet doublet, H-3 and H-4), 8.61, 8.72 (26-proton singlets, $2CMe_2$).

Anal. Calc. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 58.82; H, 8.10.

Ring-opening of epoxide A with sodium methoxide. — Epoxide A (1.15 g) in sodium methoxide (from 1 g of sodium) in methanol (75 ml) was heated for 20 h under reflux. Water (50 ml) was added to the cooled solution, the resulting solution was extracted with chloroform (3 × 50 ml), and the dried extracts were concentrated to a syrup. The syrup in light petroleum was filtered through charcoal and concentrated to a chromatographically homogeneous (t.l.c. and g.l.c.) syrup (1.02 g), $[\alpha]_D$ +12.8° (*c* 1.0, chloroform); ν_{max}^{film} 3450 cm^{-1} (OH); n.m.r. data ($CDCl_3$): τ 6.52 (3-proton singlet, OMe), 7.20 (1-proton doublet, splitting 6 Hz, OH; removed on D_2O exchange), 8.53–8.57 (12 protons, $2CMe_2$). Conventional reaction of the syrupy 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-D-altritol (**15**, 50 mg) with acetic anhydride (2 ml) in pyridine (5 ml) furnished 4-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-D-altritol (**16**, 49 mg), $[\alpha]_D$ +10.8° (*c* 1.0, chloroform); ν_{max}^{film} 1740 cm^{-1} (C=O, acetate); n.m.r. data ($CDCl_3$): τ 6.50 (3-proton singlet, OMe), 7.90 (3-proton singlet, CH_3CO), 8.55–8.70 (12 protons, $2CMe_2$).

Anal. Calc. for $C_{15}H_{26}O_7$: C, 56.59; H, 8.23. Found: C, 56.51; H, 8.15.

Ring-opening of epoxide B with sodium methoxide. — Epoxide B (0.38 g) was treated with sodium methoxide in methanol as described for epoxide A, and the syrupy product (0.31 g) crystallized on trituration with light petroleum to give 1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-D-altritol (**17**), m.p. 56.5–57.5°, $[\alpha]_D$ +1.5° (*c* 1.0, chloroform); ν_{max}^{film} 3510 cm^{-1} (OH); n.m.r. data ($CDCl_3$): τ 6.53 (3-proton singlet, OMe), 7.43 (1-proton doublet, splitting 4.5 Hz, OH; removed on D_2O exchange), 8.55–8.63 (12 protons, $2CMe_2$).

Anal. Calc. for $C_{13}H_{24}O_6$: C, 56.49; H, 8.75. Found: C, 56.33; H, 8.57. Acetylation of the foregoing compound **17** (30 mg) afforded 3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-D-altritol (**18**, 31 mg) as a syrup, $[\alpha]_D$ +25.6° (*c* 1.0, chloroform); ν_{max}^{film} 1740 cm^{-1} (C=O, acetate); n.m.r. data ($CDCl_3$): τ 6.45 (3-proton singlet, OMe), 7.90 (3-proton singlet, CH_3CO), 8.55–8.70 (12 protons, $2CMe_2$).

Anal. Calc. for $C_{15}H_{26}O_7$: C, 56.59; H, 8.23. Found: C, 56.29; H, 8.49.

3-O-Acetyl-1,2:5,6-di-O-isopropylidene-4-O-methyl-D-mannitol (**20**). — 1,2:5,6-Di-*O*-isopropylidene-3-*O*-methyl-D-mannitol[11] (**19**) (0.15 g) was acetylated as for **15** to furnish 3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-D-mannitol (**20**, 0.17 g) as a syrup, $[\alpha]_D$ +16.2° (*c* 1.0, chloroform); ν_{max}^{film} 1740 cm^{-1} (C=O, acetate); n.m.r. data ($CDCl_3$): τ 6.54 (3-proton singlet, OMe), 7.92 (3-proton singlet, CH_3CO), 8.55–8.75 (12 protons, $2CMe_2$).

Anal. Calc. for $C_{15}H_{26}O_7$: C, 56.59; H, 8.23. Found: C, 56.01; H, 8.01.

*Epimerization of 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-*D*-mannitol* (**19**). — The mannitol derivative **19** (0.55 g) was kept overnight in methyl sulfoxide (9 ml) and acetic anhydride (6 ml). The solution was diluted with chloroform (70 ml) and stirred with cooled, saturated, sodium hydrogen carbonate solution (100 ml) for 1 h. The organic layer was separated, dried and concentrated to give chromatographically homogeneous (t.l.c. and g.l.c.) 1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-D-*arabino*-3-hexulose as a syrup (0.51 g), $[\alpha]_D$ +46.5° (*c* 1.0, chloroform); *m/e* 274 (M^+), 259 (M−15); ν_{max}^{film} 1715 cm^{-1} (C=O); n.m.r. data ($CDCl_3$): τ 6.45 (3-proton singlet, OMe), 8.50–8.75 (12 protons, $2 \times CMe_2$). Sodium borohydride (0.2 g) was added to the 3-hexulose (0.1 g) in methanol (3 ml) containing a few drops of water and the solution was kept overnight. Excess of borohydride was decomposed by the addition of acetone and the solution was concentrated. The residue was dissolved in light petroleum and the filtered solution was concentrated to a syrup (101 mg), ν_{max}^{film} 3500 cm^{-1} (OH), which showed only a single peak on g.l.c. (see Table I) and a single band on t.l.c. Acetylation of the syrup (90 mg) gave a syrupy mixture of acetates (92 mg), ν_{max}^{film} 1720 cm^{-1} (C=O, acetate). Examination of the syrup by g.l.c. showed two components having the retention times (see Table I) of 3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-D-altritol (**18**, from epoxide B) and 3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-D-mannitol (**20**).

TABLE I

G.L.C. DATA FOR 1,2:5,6-DI-*O*-ISOPROPYLIDENE DERIVATIVES

Compounds[a]	T^b
3,4-Anhydro-D-mannitol (epoxide A) (**13**)	1.62
3,4-Anhydro-D-iditol (epoxide B) (**14**)	2.23
3-*O*-Methyl-D-altritol (**15**)	2.23
4-*O*-Methyl-D-altritol (**16**)	2.23
4-*O*-Acetyl-3-*O*-methyl-D-altritol (**17**)	3.46
3-*O*-Acetyl-4-*O*-methyl-D-altritol (**18**)	2.77
3-*O*-Methyl-D-mannitol (**19**)	2.23
4-*O*-Methyl-D-arabino-3-hexulose	2.08
4-*O*-Acetyl-3-*O*-methyl-D-mannitol (**20**)	3.35
(*E*)-3,4-Dideoxy-D-*threo*-hex-3-enitol (**1**)	1.00
(*Z*)-3,4-Dideoxy-D-*threo*-hex-3-enitol (**2**)	0.80
(*E*)-3,4-Dideoxy-*erythro*-hex-3-enitol (**9**)	1.00

[a] As 1,2:5,6-di-*O*-isopropylidene derivatives. [b] Retention times (*T*) are quoted relative to (*E*)-3,4-dideoxy-1,2:5,6-di-*O*-isopropylidene-D-*threo*-hex-3-enitol (**1**) on a column of silicone gum XE-60 at 180°.

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