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# SYNTHESIS OF *erythro*-3-PENTULOSE *via* A PENTITOL ISOPROPYLIDENE ACETAL AND OF L-*threo*-3-PENTULOSE *via* A BENZYLIDENE ACETAL OF A PENTITOL*

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ABSTRACT

Acetonation of xylitol yielded a mixture of 1,2 4,5-di-*O*-isopropylidenexylitol (**3**) and 2 3 4,5-di-*O*-isopropylidenexylitol (**4**) Oxidation of **3** with dimethyl sulfoxide–phosphorus pentaoxide gave ketone **5**, which was hydrolyzed to produce *erythro*-3-pentulose (**1**) The tribenzoate **9**, prepared from 1,3-*O*-benzylidene-I -arabinitol (**8**), was hydrolyzed in acid to yield a mixture of 1,4,5-tri-*O*-benzoyl-L-arabinitol (**10**) and 2,4,5-tri-*O*-benzoyl-L-arabinitol (**11**) Partial benzoylation of **11**, followed by oxidation with dimethyl sulfoxide–phosphorus pentaoxide afforded 1,2,4,5-tetra-*O*-benzoyl-L-*threo*-3-pentulose (**14**) L-*threo*-3-Pentulose (**2**) was synthesized from 2 4,5-tri-*O*-acetyl-1,3-*O*-benzylidene-L-arabinitol (**18**) After acid hydrolysis of **18**, the hydrolyzate **19** was partially acetylated to give **20** Oxidation of the resulting tetraacetate **20** with dimethyl sulfoxide–phosphorus pentaoxide, followed by hydrolysis yielded **2** From both **1** and **2**, 1-deoxy-(2,4-dinitrophenyl)osazones were obtained that were purified and characterized as the acetates **7** and **23**

## INTRODUCTION

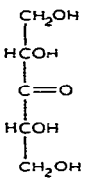
It has been reported that oxidation of pentitols with mercuric acetate gives a mixture from which 3-pentuloses have been isolated[1,2] Formation of *erythro*-3-pentulose (**1**) and D-*threo*-3-pentulose upon treatment of D-arabinose and D-xylose in boiling pyridine has also been reported[3] The synthesis of **1** by oxidation of 1,5-di-*O*-benzoyl-2 4-*O*-methylenexylitol and subsequent hydrolysis, without isolation of the final product, has been described[4] We have applied stereospecific acetonation of heptitols for the synthesis of DL- and D-*gluco*-3-heptulose[5], D-*manno*-3-heptulose[6], and D-*ido*-3-heptulose[6]

We have now synthesized 3-pentuloses *via* analogous oxidation of pentitol diisopropylidene acetals, and obtained **1** L-*threo*-3-Pentulose (**2**) was also synthesized from 1,3-*O*-benzylidene-L-arabinitol

*Part XI of the Series Coriose and Related Compounds For Part X, see ref 6

RESULTS AND DISCUSSION

Acetonation of xylitol gave two diacetals that were isolated by column chromatography A deuterium-exchangeable, broad doublet in the $^1$H-n m r. spectrum of the minor product showed the presence of a secondary hydroxyl group and the structure 1,2 4,5-di-*O*-isopropylidenexylitol (**3**) was assigned The major product contained a primary hydroxyl group, as judged by a deuterium-exchangeable triplet in the $^1$H-n m r spectrum, and it was assigned the structure 2,3 4,5-di-*O*-isopropylidenexylitol (**4**), a compound obtained as the sole product from isopropylidenation of xylitol[7–9] Oxidation of **3** with dimethyl sulfoxide–phosphorus pentaoxide gave a syrupy ketone The $^1$H-n m r spectrum of the ketone was in accord with the sym-



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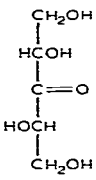

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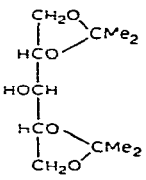

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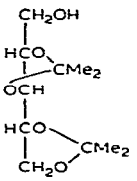

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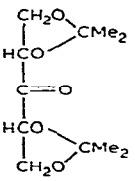

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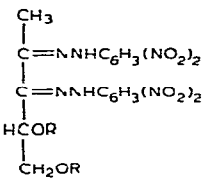

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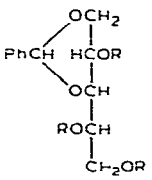

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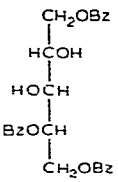

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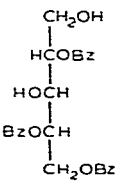

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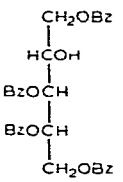

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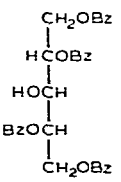

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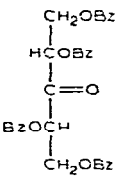

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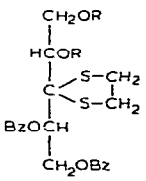

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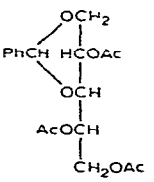

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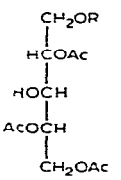

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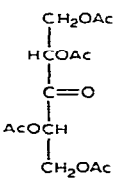

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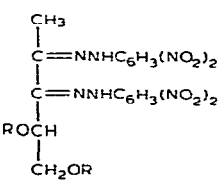

22 R = H
23 R = Ac

metrical structure, 1,2 4,5-di-*O*-isopropylidene-*erythro*-3-pentulose (**5**) This ketone was hydrolyzed in mineral acid, and the sole product was isolated by preparative paper-chromatography, giving the syrupy sugar **1**, which showed, by g l c of its trimethylsilyl derivative, a single peak the latter exhibited an ion peak at *m/e* 438 ($M^+$) and its mass-spectral pattern was identical with that of *erythro*-3-pentulose[2], by g l c –mass spectrometry The results of reduction with sodium borohydride also accorded with the structure **1** attributed Treatment of **1** with (2 4-dinitrophenyl)-hydrazine in warm, 2M hydrocnloric acid yielded an orange-colored 1-deoxy-(2,4-dinitrophenyl)osazone (**6**) in a way analogous to that of coriose[10], DL-*gluco*-3-heptulose[5], and other 3-ketoses[11] The diacetate **7** was produced from **6** Oxidation of **4**, followed by hydrolysis, yielded DL-xylose

The synthesis of L-*threo*-3-pentulose was initially attempted by a similar route, starting from L-arabinitol However, as the two diisopropylidene acetals from L-arabinitol were not isolatable by t l c , a second attempt at synthesis was performed as follows The perbenzoate(**9**) from 1,3-*O*-benzylidene-L-arabinitol[12] (**8**) was hydrolyzed in acid to yield a mixture of a crystalline product (**10**) in lower yield and higher mobility in t l c and a syrupy product (**11**) of higher yield and lower mobility in t l c , which were isolated by preparative t l c The $^1$H-n m r spectra of these two products showed the presence of three benzoyl groups The $^1$H-n m r spectrum of **11** also showed downfield shifts of H-2 H-4 and H-5 The assignments of these protons, which were confirmed by decoupling, together with other protons, indicated **11** to be 2 4,5-tri-*O*-benzoyl-L-arabinitol The $^1$H-n m r data for **10**, likewise confirmed by decoupling showed downfield shifts of H-1, H-4, and H-5, indicating **10** to be 1,4 5-tri-*O*-benzoyl-L-arabinitol The ratio of **10** to **11** observed in t l c increased upon hydrolysis either for a prolonged time or at an elevated temperature The tribenzoate **11** was usually accompanied by **10**, even after repeated purification by preparative t l c , presumably the rearrangement occurred during purification Partial benzoylation of **11** with one molar equivalent of benzoyl chloride yielded a mixture of crystalline 1,3,4 5-tetra-*O*-benzoyl-L-arabinitol (**12**) and syrupy 1,2,4,5-tetra-*O*-benzoyl-L-arabinitol (**13**) These assignments were based on $^1$H-n m r spectra and decoupling experiments Upon isolation, syrupy **13** was always accompanied by **12**, whose ratio to **13** increased upon keeping the mixture The impure, syrupy tetrabenzoate **13** was oxidized with dimethyl sulfoxide–phosphorus pentaoxide to give the crystalline ketone **14** The $^1$H-n m r spectrum of **14** showed downfield shifts of two protons, assignable to H-2 and H-4, and the mass spectrum exhibited a fragment-ion (*m/e* 269) formed by cleavage of a C–C bond at C-2–C-3 or C-3–C-4 The structure of **14** was therefore assigned as 1 2 4,5 tetra-*O*-benzoyl-L-*threo*-3-pentulose

As the production of L-*threo*-3-pentulose directly by hydrolysis of **14** was expected to be accompanied by a Lobry de Bruyn–Alberda van Ekenstein transformation, protection of the carbonyl group by thioacetal formation was performed with ethanedithiol and boron trifluoride etherate to give **15** Thioacetal **15**, although only partially purified, was methanolyzed to give the crystalline, debenzoylated

thioacetal **16** However, attempts to cleave the thioacetal group in **16** and also in the tetraacetate **17**, either by treatment with mercuric chloride–cadmium carbonate, or by acid hydrolysis, were unsuccessful

The synthesis of L-*threo*-3-pentulose was then attempted *via* crystalline 2,4,5-tri-*O*-acetyl-1,3-*O*-benzylidene-L-*threo*-arabinitol (**18**), which was prepared from **8** Acid hydrolysis of **18** yielded a syrupy hydrolyzate (**19**) that showed in the $^1$H-n m r spectrum (in dimethyl sulfoxide-$d_6$) a deuterium-exchangeable signal corresponding to two hydroxyl protons, and also (in chloroform-*d*) three acetyl signals and a proton ($\delta$ 5 00) at C-2 bearing an acetoxyl group A broad signal at $\delta$ 3 83 which sharpened to form a doubled doublet upon addition of deuterium oxide, was assigned to the proton at C-3 carrying a free hydroxyl group These data, together with assignments of other protons in the $^1$H-n m r spectrum, indicate that 2,4 5-tri-*O*-acetyl-L-arabinitol had been formed upon hydrolysis of **18** without rearrangement of acetyl groups Partial acetylation of **19** with one molar equivalent of acetyl chloride in pyridine yielded syrupy 1,2,4,5-tetra-*O*-acetyl-L-arabinitol (**20**) Oxidation of **20** with dimethyl sulfoxide–phosphorus pentaoxide gave a syrupy ketone, 1,2,4,5-tetra-*O*-acetyl-L-*threo*-3-pentulose (**21**), the $^1$H-n m r spectrum of which exhibited a similar overall pattern to that of **14**, and the $M^+$ (*m/e* 318) ion-peak in the mass spectrum The ketone **21** was hydrolyzed with 1 5% sulfuric acid in methanol to yield syrupy **2** The *O*-trimethylsilyl derivative of this sugar showed a single peak in g l c . and the mass spectrum obtained by g l c –mass spectrometry was identical to that of **1** except for the intensities of the fragment ions Sugar **2** was also reduced with sodium borohydride to give arabinitol Treatment of **2** with a solution of (2,4-dinitrophenyl)-hydrazine in 2M hydrochloric acid yielded the optically active 1-deoxy-(2,4-dinitrophenyl)osazone (**22**), whose acetate **23** was identical with the optically inactive acetate **7** of the 1-deoxy-(2,4-dinitrophenyl)osazone from **1**, by i r and $^1$H-n m r spectra These results show that the sugar synthesized is L-*threo*-3-pentulose

## EXPERIMENTAL

*General* — $^1$H-N m r spectra were determined at 90 MHz with a Hitachi R-22 instrument and chemical shifts ($\delta$) are given in p p m relative to tetramethylsilane as internal standard Mass spectra were obtained with a Shimadzu-LKB-9000 gas chromatograph–mass spectrometer using 2 m × 3 mm (i d ) glass columns containing 1% or 1 5% OV-1, or 2% OV-17 on 80–100 mesh Chromosorb W (HMDS), or by using a direct-inlet system (ion-source temperature 250°, separator temperature 220° electron energy 70 eV) $R_{Glc}$ is the retention time relative to that of α-D-glucose T l c and preparative t l c were performed on silica gel, Wako B-10, developing with solvent *A* (8 2 benzene–acetone) and detection was effected with conc sulfuric acid Column chromatography was performed on silica gel, Wako C-200, developing with chloroform, dichloromethane, or solvent *B* (benzene–acetone, gradient, up to 3%) Paper chromatography (p c ) and preparative p c were carried out with solvent *C* (6 4 3 1-butanol–pyridine–water), solvent *D* (4 1 2 1 1-butanol–ethanol–water), and

solvent *E* (4 1 5 1-butanol–acetic acid–water) Detection was effected with Tollens reagent, orcinol, or potassium periodate–benzidine reagent Evaporation of solutions was effected *in vacuo* under 40° Organic extracts were dried with magnesium sulfate

*1,2 4,5-Di*-O-*isopropylidenexylitol* (**3**) *and 2,3 4,5-di*-O-*isopropylidenexylitol* (**4**) — Anhydrous cupric sulfate (10 0 g) and conc sulfuric acid (2 0 ml) were added to a suspension of xylitol (22 8 g) in dry acetone (300 ml) with stirring at room temperature The mixture was stirred for 18 h, filtered, and the filtrate was neutralized by stirring with anhydrous potassium carbonate (20 0 g), and the mixture was filtered The filtrate was concentrated to a syrup (22 2 g) that showed in t l c a small spot ($R_F$ 0 45, **3**) and a large spot ($R_F$ 0 40, **4**) These two products were isolated by silica-gel column chromatography (solvent *B*) to yield syrupy **3** (250 mg) and **4** (13 3 g) which was crystallized from hexane to give colorless needles, m p 32–34°

Data for **3** *m/e* 217 (M − 15), $\nu_{max}^{CHCl_3}$ 3550 (OH), 1380 and 1370 $cm^{-1}$ ($Me_2C$) $^1$H-n m r (chloroform-*d*) $\delta$ 1 34 (s, 2 Me), 1 41 (s, 2 Me), 2 40 (d *J* 5 Hz, 1 H, D exchangeable), and 3 37–4 29 (m, 7 H)

*Anal* Calc for $C_{11}H_{20}O_5$ C, 56 88, H, 8 68 Found C 56 69, H, 8 63

Data for **4** *m/e* 217 (M − 15), $\nu_{max}^{CHCl_3}$ 3450 (OH), 1380 and 1370 $cm^{-1}$ ($Me_2C$), $^1$H-n m r (dimethyl sulfoxide-$d_6$) $\delta$ 1 29–1 33 (4 Me), 3 78–4 22 (m, 7 H) and 4 80 (t, *J* 6 Hz, 1 H, D exchangeable)

*Anal* Calc for $C_{11}H_{20}O_5$ C, 56 88, H, 8 68 Found C, 57 00, H 8 75

*1 2 4,5-Di*-O-*isopropylidene*-erythro-*3-pentulose* (**5**) — Phosphorus pentaoxide (50 mg) was added to an ice-cooled solution of **3** (250 mg) in dry dimethyl sulfoxide (10 ml) with stirring After dissolution of the phosphorus pentaoxide, the solution was stirred for 18 h at room temperature, and then poured into ice–water The mixture was extracted with dichloromethane, the dichloromethane extracts were washed with 10% aqueous sodium hydrogencarbonate and water dried, and filtered The filtrate was evaporated to a syrup that was chromatographed on a column of silica gel eluted with dichloromethane, to yield syrupy **5** (80 mg), *m/e* 215 (M − 15), $\nu_{max}^{CHCl_3}$ 1735 $cm^{-1}$ (C=O) $^1$H-n m r (chloroform-*d*) $\delta$ 1 37 (s, 2 Me), 1 44 (s, 2 Me) 3 98 (dd, $J_{1,1'} = J_{5,5'} = 9$ Hz, $J_{1,2} = J_{4,5} = 6'$ Hz, H-1 and H-5), 4 31 (dd, $J_{1',2} = J_{4',5'} = 8$ Hz, H-1′ and H-5′) and 4 78 (dd, H-2 and H-4)

*Anal* Calc for $C_{11}H_{18}O_5$ C, 57 38, H, 7 88 Found C, 57 51, H, 7 66

erythro-*3-Pentulose* (**1**) — Sulfuric acid (1%, 5 ml) was added to a solution of **5** (60 mg) in acetone (1 ml) After warming for 5 h at 55°, water was added to bring the volume of the mixture to 10 ml and it was then extracted with dichloromethane (10 ml × 3) The aqueous layer was neutralized with saturated aqueous barium hydroxide, and then centrifuged The supernatant liquor was evaporated to a syrup that was dissolved in methanol, and clarified by filtration The filtrate was evaporated and the residue was purified by preparative p c (solvent *C*) to give syrupy **1** (39 mg) $R_F$ 0 46 (solvent *C*), 0 31 (solvent *D*), and 0 24 (solvent *E*) Detection was effected with Tollens reagent Unlike 3-heptuloses and 3-hexuloses, this 3-pentulose gave a negative orcinol test G l c of the trimethylsilyl derivative showed $R_{Glc}$ 0 41 (1 5% OV-1, 170°), g l c–m s *m/e* 438 ($M^+$)

*Anal* Calc for $C_5H_{10}O_5 \cdot H_2O$ C, 35 71, H, 7 19 Found C, 35 45, H, 7 33

*Reduction of* erythro-*3-pentulose with sodium borohydride* — Sodium borohydride (1 mg) was added to a solution of **1** (5 mg) in water (1 ml) under ice-cooling The mixture was refrigerated overnight, and then passed through a column of IR-120 ($H^+$) resin, and evaporated Methanol (1 ml) was added to the residue, which was evaporated, and this procedure was repeated five times The resulting syrup was trimethylsilylated for g l c , $R_{Glc}$ 0 34 (2 5% OV-17, 150°), $R_{Glc}$ 0 42 (xylitol) and 0 46 (ribitol) (1% OV-1, 150°)

*1-Deoxy*-erythro-*3-pentulose (2 4-dinitrophenyl)osazone diacetate* (**7**) — A warm solution of (2,4-dinitrophenyl)hydrazine (50 mg) in a mixture of 2M hydrochloric acid (10 ml) and ethanol (1 ml) was added to a solution of **1** (28 mg) in 2M hydrochloric acid (2 ml) The resulting mixture was warmed for 1 h in a boiling-water bath, and the crystals deposited were filtered off (**6**, 20 mg) Acetic anhydride (0 5 ml) was added to a solution of this product in pyridine (0 5 ml), the solution was kept overnight at room temperature, and it was then poured into ice-water The mixture was extracted with dichloromethane, the extract washed successively with 5% hydrochloric acid, saturated aqueous sodium hydrogencarbonate, and water, and dried Evaporation of the solvent yielded a crude syrup that was purified by column chromatography on silica gel (solvent *B*) to give a product that crystallized from ethanol (0 5 ml), and was recrystallized twice from ethanol to give orange needles (**7**, 12 5 mg) m p 143–145° (dec) $\nu_{max}^{CHCl_3}$ 3200–3600 (NH), 1745 $cm^{-1}$ (C=O), $\lambda_{max}^{CHCl_3}$ 390 (log ε 4 43), 437 nm (4 43), $^1$H-n m r (chloroform-*d*) δ 1 94 (s, Ac), 2 25 (s, Ac) 2 43 (s, Me–C=N–), 4 53 (dd, $J_{5,5'}$ 8 Hz, $J_{4,5'}$ 5 Hz, H-5), 4 58 (dd, $J_{4,5}$ 4 Hz, H-5′), 6 90 (dd, H-4), and 7 96–9 22 (6 aromatic protons of 2,4-dinitrophenyl), 11 46 (s, H-bonded NH) and 12 77 (s H-bonded NH)

*Anal* Calc for $C_{21}H_{20}N_8O_{12}$ C, 43 75, H 3 50, N, 19 44 Found C, 43 50, H, 3 58, N, 19 41

*2 4 5-Tri-O-benzoyl-1 3-O-benzylidene-*L*-arabinitol* (**9**) — This compound was prepared from 1,3-*O*-benzylidene-L-arabinitol[12] in essentially the same way as for the synthesis of 1,3-*O*-benzylidene-2 4,5-tri-*O*-benzoyl-D-arabinitol[13] m p 138–139°, $[\alpha]_D^{15}$ +139° (*c* 0 41 chloroform), $\nu_{max}^{Nujol}$ 1720 $cm^{-1}$ (C=O), $^1$H-n m r (chloroform-*d*) δ 4 22 (dd $J_{1,1'}$ 12 Hz $J_{1,2}$ 2 Hz H-1), 4 51 (dd, $J_{1',2}$ 2 Hz, H-1′), 4 60 (dd, $J_{3,4}$ 9 Hz, $J_{2,3}$ 2 Hz H-3), 4 71 (dd, $J_{5,5'}$ 12 Hz, $J_{4,5'}$ 5 Hz H-5), 4 91 (dd, $J_{4,5}$ 4 Hz H-5′), 5 20 (m, H-2), 5 74 (s, $C_6H_5CHO_2$) 5 83 (m H-4) and 7 27–8 15 (m, 20 H, 3 Bz and $C_6H_5$) *m/e* 552 ($M^-$)

*Anal* Calc for $C_{33}H_{28}O_8$ C, 71 73, H, 5 11 Found C, 71 61, H, 5 00

*Acid hydrolysis of 2,4,5-tri-O-benzoyl-1,3-O-benzylidene-*L*-arabinitol* — Sulfuric acid (1%) in methanol (20 ml) was added to a solution of **9** (3 0 g) in chloroform (15 ml) and the mixture was kept overnight, and then extracted with chloroform The extract was washed with saturated aqueous sodium hydrogencarbonate and water, and dried Evaporation of the solvent yielded a syrup (2 3 g) Preparative t l c of this syrup (150 mg) gave crystalline **10**, which was recrystallized from ethanol to give colorless needles, m p 104–105° (20 mg), and syrupy **11** (90 mg) containing a small

amount of **10** Data for **10** $[\alpha]_D^{15}$ +20 8° (*c*, 0 48, chloroform), $\nu_{max}^{Nujol}$ 3450, 1720 $cm^{-1}$, $^1$H-n m r (chloroform-*d*) $\delta$ 3 05–3 22 (broad band, 2 H, D exchangeable), 4 00 (m, H-2 and H-3), 4 51 (d, $J_{1,2} = J_{1',2} = 7$ Hz, H-1 and H-1′), 4 86 (d, $J_{4,5}$ 4 Hz, H-5 and H-5′), 5 52 (m, H-4), and 7 28–8 12 (m, 15 H, 3 Bz) Irradiation of the multiplet at $\delta$ 5 52 converted the doublet at $\delta$ 4 86 into a singlet, and irradiation of the multiplet at $\delta$ 4 00 converted the doublet at $\delta$ 4 51 into a singlet

*Anal* Calc for $C_{26}H_{24}O_8$ C, 67 23, H, 5 21 Found C, 66 85 H, 5 26

Data for **11** $^1$H-n m r (chloroform-*d*) $\delta$ 4 05 (d, $J_{1,2} = J_{1',2} = 5$ Hz, H-1 and H-1′), 4 38 (dd, $J_{3,4}$ 9 Hz, $J_{2,3}$ 3 Hz, H-3), 4 81 (d, $J_{4,5} = J_{4',5'} = 4$ Hz, H-5 and H-5′), 5 32 (dt, H-2), and 5 51 (m H-4) Irradiation at $\delta$ 5 32 converted the doublet at $\delta$ 4 05 into a singlet, and the doubled doublet at $\delta$ 4 38 into a doublet ($J$ 9 Hz) Irradiation at $\delta$ 4 38 converted the doubled triplet at $\delta$ 5 32 into a triplet, and increased the height of the multiplet at $\delta$ 5 51 Irradiation at $\delta$ 5 51 converted the doublet at $\delta$ 4 81 into a singlet

*Partial benzoylation of 2,4,5-tri-*O*-benzoyl-*L*-arabinitol* (**11**) — Benzoyl chloride (0 5 g) was added to a stirred, ice-cooled solution of **11** (2 34 g) containing a small amount of **10** in pyridine (20 ml) and the mixture was kept overnight The mixture was then poured into ice–water and extracted with chloroform The chloroform solution was washed successively with 5% hydrochloric acid water, saturated aqueous sodium hydrogencarbonate, and water, and then dried Evaporation of the solvent yielded a syrup (2 3 g) that showed in t l c a smaller spot of higher mobility (**12**) and a larger spot of lower mobility (**13**) After column chromatography (chloroform) compound **12** could be recrystallized from ethanol as colorless needles m p 177–179° (150 mg), and a syrup (**13**, 711 mg) was also isolated

Data for **12** $[\alpha]_D^{15}$ +30 3° (*c* 0 33 chloroform), $\nu_{max}^{Nujol}$ 3450, 1720–1700 $cm^{-1}$, $^1$H-n m r (chloroform-*d*) $\delta$ 3 10 (1 H D exchangeable), 4 22–4 49 (m, H-1, H-1′ and H-2), 4 57 (dd, $J_{5,5'}$ 13 Hz, $J_{4,5}$ 6 Hz H-5), 4 99 (dd $J_{4,5'}$ 3 Hz, H-5′), 5 83 (m H-3 and H-4), and 7 25–8 10 (m, 4 Bz) Irradiation at $\delta$ 5 83 converted the two doubled doublets at $\delta$ 4 57 and 4 99 into doublets ($J$ 13 Hz) *m/e* 551 (M − 17)

*Anal* Calc for $C_{33}H_{28}O_9$ C 69 71, H 4 96 Found C, 69 39, H, 5 25

Data for **13** *m/e* 551 (M − 17), $^1$H-n m r (chloroform-*d*) $\delta$ 3 68 (broad D exchangeable signal, 1 H), 4 35 (br t converted into a doubled doublet $J_{3,4}$ 8 Hz, $J_{2,3}$ 2 Hz, upon addition of $D_2O$, H-3), 4 50–5 00 (m, H-1, H-1′ H-5 and H-5′), 5 55 (dt, $J_{4,5'}$ 4 Hz, H-4), 5 77 (dq, $J_{1,2}$ 7 Hz, $J_{1',2}$ 6 Hz H-2), and 7 22–8 07 (m 4 Bz) Irradiation of the doubled quartet at $\delta$ 5 77 converted the broad triplet at $\delta$ 4 35 into a triplet, and irradiation of the doubled triplet at $\delta$ 5 55 converted the broad triplet into a broad doublet ($J$ 7 Hz)

*Oxidation of* **13** *with dimethyl sulfoxide–phosphorus pentaoxide* — Phosphorus pentaoxide (0 40 g) was slowly added to an ice-cooled solution of **13** (0 70 g) in dimethyl sulfoxide (15 ml) with stirring The mixture was then stirred for 1 h at 60° and after confirming the disappearance of **13** by t l c , it was poured into ice–water The crystals deposited were filtered off, and recrystallized from ethanol to give **14** (562 mg) The mother liquor was extracted with chloroform, and the chloroform

solution was washed with saturated, aqueous sodium hydrogencarbonate and water, and dried Evaporation of the solvent yielded a syrup that was crystallized and then recrystallized from ethanol, (74 mg) total yield of **14**, 636 mg, m p 142–143°, $[\alpha]_D^{15}$ +40 5° (*c* 0 37, chloroform). $\nu_{max}^{Nujol}$ 1725, 1710, 1600, and 1580 $cm^{-1}$, $^1$H-n m r (chloroform-*d*) 4 93 (dd, $J_{1,1} = J_{5\ 5} = 12\ 5$ Hz, $J_{1\ 2} = J_{4\ 5} = 6$ Hz, H-1 and H-5), 5 13 (dd, $J_{1\ 2} = J_{4,5} = 4$ Hz, H-1′ and H-5′). 6 07 (dd, H-2 and H-4) and 7 25–8 09 (m 4 Bz). *m/e* 444 (M−BzOH)

*Anal* Calc for $C_{33}H_{26}O_9$ C 69 96, H, 4 63 Found C, 69 64, H, 4 58

*Ethane dithioacetal* **15** *from* **14** — Boron trifluoride diethyl etherate (13 ml) was added to a solution of **14** (3 9 g) in 1,2-ethanedithiol (13 ml) The mixture was kept overnight. poured into ice–water, and extracted with chloroform The chloroform solution was washed with saturated aqueous sodium hydrogencarbonate and water and dried Evaporation of the solvent to yield a syrup was followed by further evacuation at 115° *in vacuo* to give a syrup (**15** 3 2 g) that showed a single spot on t l c , although some contamination was found by the $^1$H-n m r spectrum $^1$H-n m r (chloroform-*d*) $\delta$ 3 44 (s –S–$CH_2CH_2$–S–) 4 89 (dd $J_{1\ 1} = J_{5\ 5} = 12$ Hz $J_{1\ 2} = J_{4\ 5} = 9$ Hz H-1 and H-5), 5 14 (dd, $J_{1\ 2} = J_{4\ 5} = 3$ Hz H-1′ and H-5′) 6 12 (dd H-2 and H-4), and 7 28–8 13 (m, 4 Bz)

*Methanolysis of* **15** — To a solution of **15** (3 0 g) in chloroform (1 ml), was added 0 25M sodium methoxide in methanol (40 ml) and the mixture was kept for 6 h at 40° After disappearance of **15** was confirmed in t l c the mixture was poured into ice–water (50 ml), and extracted with chloroform (20 ml) three times The aqueous layer was passed through a column of IR-120 ($H^+$) resin and the eluate was evaporated to give a syrup that was crystallized and recrystallized from methanol to yield colorless needles of **16** (500 mg) m p 155–156° $[\alpha]_D^{15}$ −68 1° (*c* 0 22, water) $R_F$ 0 62 (solvent C) $\nu_{max}^{Nujol}$ 3350–3200 $cm^{-1}$ (OH). g l c of the trimethylsilyl derivative $R_{Glc}$ 2 97 (2% OV-17 200°) g l c–m s of the trimethylsilyl derivative *m e* 514 ($M^-$) 499 (M−15) 411 (M−$CH_2OSiMe_3$) and 309 (M−CHOSi$Me_3$−$CH_2OSiMe_3$)

*Anal* Calc for $C_7H_{14}O_4S_2$ C 37 15 H, 6 24 Found C 37 05 H, 6 04

*Tetraacetate* **17** *from* **16** — A mixture of **16** (480 mg), pyridine (5 ml), and acetic anhydride (5 ml) was kept overnight, poured into ice–water, and extracted with chloroform The chloroform solution was washed with 5% hydrochloric acid saturated aqueous sodium hydrogencarbonate, and water, and dried Evaporation of the solvent yielded a syrup (**17** 780 mg), $[\alpha]_D^{26}$ +7 3° (*c* 1 32 chloroform), $\nu_{max}^{CHCl_3}$ 1740 $cm^{-1}$ $^1$H-n m r (chloroform-*d*) $\delta$ 2 00 (s, 2 Ac), 2 04 (s, 2 Ac), 3 30 (s, –$SCH_2CH_2S$–) 4 31 (dd $J_{1\ 1} = J_{5\ 5} = 12$ Hz, $J_{1\ 2} = J_{4\ 5} = 8$ Hz, H-1 and H-5), 4 76 (dd $J_{1\ 2} = J_{4\ 5} = 2\ 5$ Hz H-1′ and H-5′), and 5 51 (dd, H-2 and H-4), *m/e* 394 ($M^-$)

*Anal* Calc for $C_{15}H_{22}O_8S_2$ C, 45 67, H, 5 62 Found C, 45 38, H, 5 71

*2,4,5-Tri-O-acetyl-1 3-O-benzylidene-*L*-arabinitol* (**18**) — Acetylation of **8** (7 6 g) was effected with acetic anhydride and pyridine, and the product was recrystallized from ethanol–petroleum ether to give crystalline **18** (7 5 g), m p 121–123° $[\alpha]_D^{15}$ +85 7° (*c* 0 35, chloroform), $\nu_{max}^{Nujol}$ 1730 $cm^{-1}$ (C=O), $^1$H n m r (chloroform-

*d*) $\delta$ 2 00 (s, Ac), 2 03 (s, Ac), 2 09 (s, Ac), 4 08 (dd, $J_{1,1}$ 13 Hz, $J_{1,2}$ 2 Hz, H-1), 4 21 (dd, $J_{5,5}$ 12 Hz $J_{4,5}$ 3 Hz, H-5), 4 31 (dd $J_{1,2}$ 2 Hz, H-1'), 4 43 (dd, $J_{4,5}$ 3 Hz, H-5'), 4 87 (br s, H-2), 5 20–5 35 (m, H-4), 5 62 (s, $C_6H_5CHO_2$), and 7 25–7 55 (m, $C_6H_5$), *m/e* 366 ($M^+$)

*Anal* Calc for $C_{18}H_{22}O_8$ C, 59 12 H, 6 05 Found C, 59 12, H, 6 11

*Acid hydrolysis of* **18** — Concentrated hydrochloric acid (1 ml) was added to a solution of **18** (2 0 g) in acetic acid (60 ml) The solution was stirred for 6 h at room temperature and then poured into ice–water The mixture was extracted with chloroform, and the chloroform solution was successively washed with water, saturated aqueous sodium hydrogencarbonate and water, and dried Evaporation gave a syrup that was passed through a column of silica gel (solvent *B*) to yield the syrupy triacetate **19** (780 mg) $\nu_{max}^{CHCl_3}$ 3500 (OH), 1740 $cm^{-1}$ (C=O), $^1$H-n m r (chloroform-*d*) $\delta$ 2 06 (s, Ac), 2 08 (s Ac), 2 09 (s, Ac) 3 83 (br s converted into a doubled doublet, $J_{3,4}$ 10 Hz, $J_{2,3}$ 2 Hz, upon addition of $D_2O$, H-3), 4 03–4 36 (m, H-1 and H-1'), 4 33 (dd, $J_{5,5}$ 10 Hz $J_{4,5}$ 6 Hz, H-5), 4 44 (dd, $J_{4,5}$ 5 Hz, H-5 ) 5 00 (m H-2) and 5 28 (m H-4)

*Anal* Calc for $C_{11}H_{18}O_8$ C 47 48 H, 6 52 Found C 48 02 H, 6 29

*1 2 4,5-Tetra-*O*-acetyl-*L*-arabinitol* (**20**) — Acetyl chloride (0 10 ml) was added to an ice-cooled solution of **19** (0 40 g) in pyridine (10 ml), and after keeping overnight at room temperature the mixture was poured into ice–water The mixture was then extracted with chloroform and the extract was washed with saturated aqueous sodium hydrogencarbonate and water, and dried Evaporation of the solvent yielded a syrup (380 mg) that was passed through a column of silica gel to give **20** as a purified syrup (300 mg) $[\alpha]_D^{20}$ −15 9° (*c* 2 76, chloroform), $\nu_{max}^{CHCl_3}$ 3450, 1750 $cm^{-1}$, $^1$H n m r (chloroform-*d*) $\delta$ 2 03–2 07 (4 Ac), 3 08–3 26 (broad signal D exchangeable), 3 84 (broad signal converted into dd $J_{3,4}$ 9 Hz $J_{2,3}$ 2 Hz upon addition of $D_2O$, H-3), 4 02–4 54 (m H-1 H-1 , H-5 and H-5') 4 98 (m, H-4) and 5 23 (dq, $J_{1,2}$ 8 Hz, $J_{1,2}$ 6 Hz H-2) *m/e* 303 (M − 17)

*Anal* Calc for $C_{13}H_{20}O_9$ C 47 55, H 8 60 Found C, 47 47, H, 8 59

*1 2 4 5-Tetra-*O*-acetyl-*L*-threo-3-pentulose* (**21**) — Phosphorus pentaoxide (100 mg) was slowly added with stirring to an ice-cooled solution of **20** (170 mg) in dimethyl sulfoxide (10 ml) and the mixture was stirred for 3 h at 60–70° After confirming by t l c that consumption of **20** was complete, the mixture was poured into ice–water and extracted with chloroform The chloroform solution was washed with saturated aqueous sodium hydrogencarbonate and water, and dried Evaporation of the solvent yielded a syrup that was passed (chloroform) through a column of silica gel to give syrupy **21**, which showed a single spot on t l c , although some contamination was shown in the $^1$H-n m r spectrum (chloroform-*d*) $\delta$ 2 07–2 14 (4 Ac), 4 28 (dd, $J_{1,1} = J_{5,5} = 13$ Hz, $J_{1,2} = J_{4,5} = 7$ Hz, H-1 and H-5), 4 64 (dd, $J_{1,2} = J_{4,5} = 4$ Hz, H-1' and H-5'), and 5 56 (dd, H-2 and H-4), *m/e* 318 ($M^+$), 259 (M − 59)

L-threo-*3-Pentulose* (**2**) — A solution of **21** (85 mg) in 1 5% sulfuric acid in methanol (5 ml) was kept overnight at room temperature, diluted with water (10 ml),

and neutralized with aqueous barium hydroxide The precipitate was centrifuged off, and the supernatant liquor was concentrated to a syrup that was purified by preparative p c (solvent *C*) to afford syrupy **2** (18 mg), $[\alpha]_D^{29}$ +81 5° (*c* 1 85, water), $R_F$ 0 38 (solvent *C*), 0 54 (solvent *D*), 0 32 (solvent *E*), g l c of the trimethylsilyl derivative $R_{Glc}$ 0 25 (1% OV-1, 180°), m s of the trimethylsilyl derivative *m/e* 438 ($M^+$) and 205

Sodium borohydride (2 5 mg) was slowly added to a solution of **2** (5 mg) in water (1 ml), the solution was kept overnight at room temperature, and then passed through a column of IR-120 ($H^+$) resin (1 ml) The eluate was evaporated to a syrup Methanol was added to this syrup and distilled off *in vacuo* This procedure was repeated five times to yield a syrup that was identified as arabinitol by p c (solvents *C* and *D*), and by g l c (1% OV-1, 160°) of the trimethylsilyl derivative

*1-Deoxy*-L-threo-*3-pentulose (2,4-dinitrophenyl)osazone diacetate* (**23**) — A solution of (2,4-dinitrophenyl)hydrazine (40 mg) in a mixture of 2M hydrochloric acid (5 ml) and ethanol (1 ml) was added to a solution of **2** (10 mg) in 2M hydrochloric acid (5 ml) The solution was warmed for 1 h in a boiling-water bath whereupon it deposited orange crystals (**22**) that filtered from the hot solution The crystals were dissolved in pyridine (0 5 ml), acetic anhydride (0 5 ml) was added, and after keeping at room temperature overnight, the mixture was poured into ice–water, and extracted with chloroform The chloroform solution was washed successively with 5% hydrochloric acid, water, saturated aqueous sodium hydrogencarbonate, and water After drying, the solvent was evaporated, and the residue was crystallized and recrystallized from ethanol to yield orange, fine needles, $[\alpha]_D^{29}$ +58 8° (*c* 0 17, chloroform) The i r and $^1$H-n m r spectra were identical with those of **7**

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