Higher-carbon Sugars. Part 12.[1] The Synthesis of New Octitols from D-Glucose and D-Mannose *via* the Osmylation of Unsaturated Precursors[2]

John C. Barnes, John S. Brimacombe,* Abul K. M. S. Kabir, and Timothy J. R. Weakley
Chemistry Department, The University of Dundee, Dundee DD1 4HN

Catalytic osmylation of methyl (*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-*gluco*-oct-6-enopyranoside (**8**) produced a mixture of methyl 2,3,4-tri-*O*-benzyl-β-L-*threo*-D-*gluco*-octopyranoside (**9**) and the corresponding α-D-*threo*-D-*gluco* isomer (**10**) in the ratio *ca.* 3:1, respectively. After separation from the mixture as the crystalline triacetate (**11**), the regenerated triol (**9**) was transformed into L-*threo*-L-*altro*-octitol (L-*threo*-D-*gluco*-octitol) (**12**). Methyl (*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-*manno*-oct-6-enopyranoside (**17**) furnished a mixture of methyl 2,3,4-tri-*O*-benzyl-β-L-*threo*-D-*manno*-octopyranoside (**18**) and the corresponding α-D-*threo*-D-*manno* isomer (**19**) on catalytic osmylation. The crystalline hexa-acetate (**20**) derived from the octopyranoside (**18**) was subsequently transformed into D-*erythro*-L-*altro*-octitol (L-*threo*-D-*manno*-octitol) (**21**). Both osmylation reactions proceed in accordance with Kishi's empirical rule. The structural assignments are based on single-crystal *X*-ray analyses of the acetylated compounds (**11**) and (**20**).

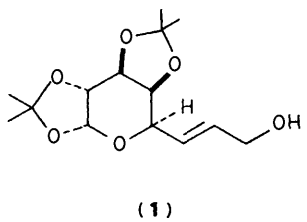
In a previous paper[3] in this series, we described the stereoselective synthesis of a number of eight-carbon sugars *via* the OsO_4-catalysed bishydroxylation of unsaturated precursors obtained from D-galactopyranose derivatives by two-carbon extension of the non-reducing end of the chain. Catalytic osmylation of (*E*)-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enopyranose (**1**), for example, furnished a mixture of 1,2:3,4-di-*O*-isopropylidene-β-L-*threo*-D-*galacto*-octopyranose (**2**) and the α-D-*threo*-D-*galacto* isomer (**3**) in the ratio *ca.* 7:1, respectively. Kishi's empirical rule[4] predicts that the stereoisomer (**2**) should preponderate in this osmylation, with the reagent approaching the least compressed conformation (**4**) about the allylic system from the direction *anti* to the pyranose ring-oxygen atom. Subsequently it was shown[5] that the catalytic osmylation of hept-5-enofuranose systems similarly proceeds in an *anti* fashion with respect to the furanose ring-oxygen atom, except where steric factors intervene through the injudicious positioning of bulky protecting groups on the substrate. Thus, whilst catalytic osmylation promotes the stereocontrolled synthesis of eight-carbon sugars possessing the D-*galacto* configuration at C-2 to C-5,[3] it is not known whether similar stereocontrol would be exerted in other series, particularly where the approach of a large electrophile like OsO_4 to heavily and bulkily substituted substrates might be impeded. In seeking to provide this information, we have examined the catalytic osmylation of methyl (*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-*gluco*-oct-6-enopyranoside (**8**) and the corresponding α-D-*manno* isomer (**17**).

Results and Discussion

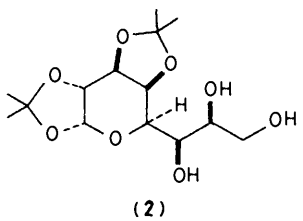
In the D-glucose series, the ascent began from methyl 2,3,4-tri-*O*-benzyl-α-D-*gluco*-hexodialdo-1,5-pyranoside (**6**),[6] which was readily obtained by Swern oxidation[7] of the alcohol (**5**). On reaction with formylmethylenetriphenylphosphorane[8] in boiling benzene, the D-*gluco* aldehyde (**6**) furnished methyl (*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-*gluco*-oct-6-enodialdo-1,5-pyranoside (**7**) in 75% yield. Alternatively, oxidation of the alcohol[6] (**5**) with pyridinium chlorochromate[9] in the presence of molecular sieves[10] gave the aldehydo derivative (**6**), which was then allowed to react with formylmethylenetriphenylphosphorane[8] at room temperature, without removal of the oxidising agent, to form the enal (**7**). The *E*-geometry assigned to this enal was clearly indicated[3,11] by the magnitude of the spin–spin coupling ($J_{6,7}$ 15.8 Hz) of the olefinic protons. Reduction of the enal (**7**) with di-isobutylaluminium hydride in methylene dichloride at 0 °C provided the (*E*)-allylic alcohol (**8**), which, on catalytic osmylation,[12] produced a mixture (76%) of methyl 2,3,4-tri-*O*-benzyl-β-L-*threo*-D-*gluco*-octopyranoside (**9**) and the corresponding α-D-*threo*-D-*gluco* isomer (**10**) in the ratio *ca.* 3:1 (determined by integration over the signals for the methoxy groups in the 360 MHz ^{1}H n.m.r. spectrum). Acetylation of this mixture afforded, as the principal product, methyl 6,7,8-tri-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-L-*threo*-D-*gluco*-octopyranoside (**11**), whose stereochemistry was established by *X*-ray crystallographic analysis (see Figure 1 and Experimental). In compliance with Kishi's formulation,[4] the hydroxy groups introduced at C-6 and C-7 on osmylation of the allylic alcohol (**8**) possess the L-*threo* configuration. Zemplén deacetylation of the triacetate (**11**) regenerated the triol (**9**), which, on removal of the protecting groups, reduction of the resulting octose, and acetylation of the crude octitol (**12**), gave L-*threo*-L-*altro*-octitol (L-*threo*-D-*gluco*-octitol) octa-acetate (**13**). Finally, L-*threo*-L-*altro*-octitol (**12**) was obtained in crystalline form following Zemplén deacetylation of the octa-acetate (**13**).

In an analogous ascent from methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside[13] (**14**), Swern oxidation[7] afforded the 6-aldehydo derivative[13,14] (**15**), which reacted with formylmethylenetriphenylphosphorane[8] in boiling benzene to give methyl (*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-*manno*-oct-6-enodialdo-1,5-pyranoside (**16**). In this instance, oxidation of the alcohol (**14**) with pyridinium chlorochromate[9] in methylene dichloride, followed by reaction *in situ* of the 6-aldehydo derivative (**15**) with the Wittig reagent,[8] gave a much cleaner product although in slightly inferior yield. The spin–spin coupling ($J_{6,7}$ 15 Hz) of the olefinic protons is consistent[3,11] with the *E*-geometry assigned to the enal (**16**), which was reduced in a straightforward manner to methyl (*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-*manno*-oct-6-enopyranoside (**17**) with di-isobutylaluminium hydride.

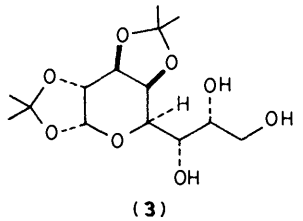
Catalytic osmylation[12] of the allylic alcohol (**17**) afforded a mixture (64%) of methyl 2,3,4-tri-*O*-benzyl-β-L-*threo*-D-*manno*-octopyranoside (**18**) and the corresponding α-D-*threo*-D-*manno* isomer (**19**) in the ratio *ca.* 4:1, respectively. Catalytic debenzylation of this mixture and acetylation of the products gave methyl 2,3,4,6,7,8-hexa-*O*-acetyl-β-L-*threo*-D-*manno*-



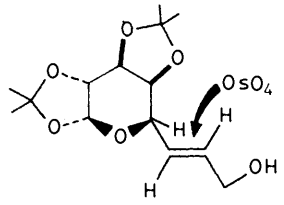
(1)



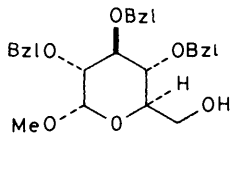
(2)



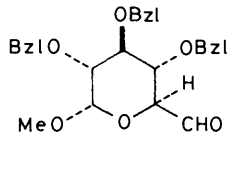
(3)



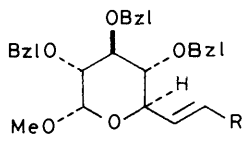
(4)



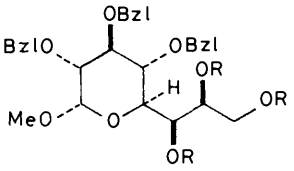
(5)



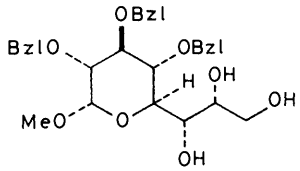
(6)



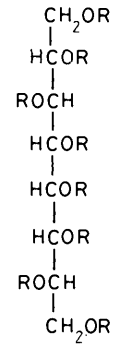
(7) R = CHO
(8) R = CH_2OH



(9) R = H
(11) R = Ac



(10)



(12) R = H
(13) R = Ac

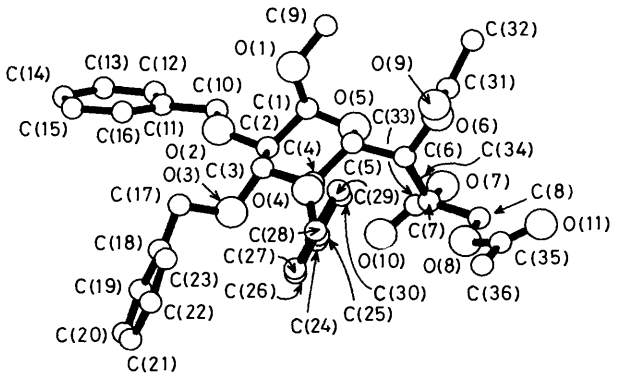


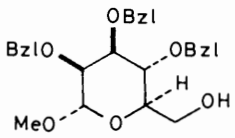
Figure 1. *X*-Ray molecular structure of methyl 6,7,8-tri-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-L-*threo*-D-*gluco*-octopyranoside (**11**)

octopyranoside (**20**) in 46% yield. A single-crystal *X*-ray analysis of the hexa-acetate (**20**) established its structure (see Figure 2 and Experimental section) and, hence, that of the triol (**18**), which had been assigned[2] previously by analogy with the osmylation of the D-*gluco* compound (**8**). Thus, the catalytic osmylation of the allylic alcohol (**17**), like that of its stereoisomer (**8**), is *anti* stereoselective[3,4] with respect to the pyranose ring-oxygen atom. Zemplén deacetylation of the hexa-acetate (**20**), acidic hydrolysis, and reduction of the resulting octose then furnished D-*erythro*-L-*altro*-octitol (L-*threo*-D-*manno*-octitol) (**21**) in crystalline form.

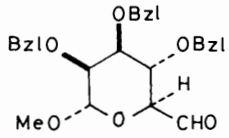
The catalytic osmylation of unsaturated precursors based on D-galactose,[3] D-glucose, and D-mannose has provided access to several new octitols, and this approach nicely complements the traditional one of ascending the series from the reducing end of the sugar chain.[15] It also has another potential advantage to exploit. Appropriate protection of the triols (**9**) and (**18**), for example, and subsequent debenzylation would yield compounds for which well-established chemistry might be used to invert the configurations of the hydroxy groups attached to the pyranose ring, thereby opening up routes to other eight-carbon sugars. Finally, our fears that the injudicious positioning of bulky protecting groups near the olefinic system might influence the stereochemical outcome of osmylation reactions seem to be justified in the light of recent work by Danishefsky and co-workers.[16] Whereas osmylation of the *C*-silylated D-*galacto* compound (**22**) yielded the predicted (Kishi) product with exceptionally high stereoselectively, with that of the related D-*gluco* compound (**23**) there was a slight preference for the anti-Kishi product. It appears that the sheer bulk of the t-butyldimethylsilyloxy group in an equatorial orientation at C-4 influences the stereochemical outcome of the reaction, perhaps by forcing the D-*gluco* compound (**23**) to react preferentially in a conformation other than that akin to (**4**).

Experimental

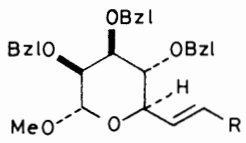
T.l.c. was performed on Kieselgel G, and spots were detected with 1% aqueous sulphuric acid. ^1H N.m.r. spectra were recorded for solutions in deuteriochloroform (internal tetramethylsilane) at 360 MHz by Edinburgh University n.m.r.



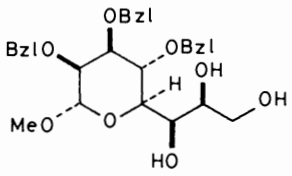
(14)



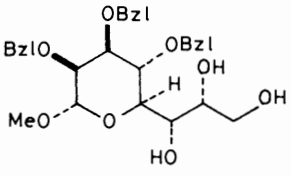
(15)



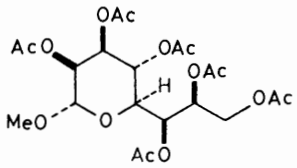
(16) R = CHO
(17) R = CH_2OH



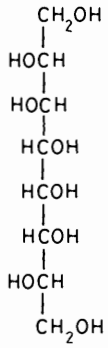
(18)



(19)



(20)



(21)

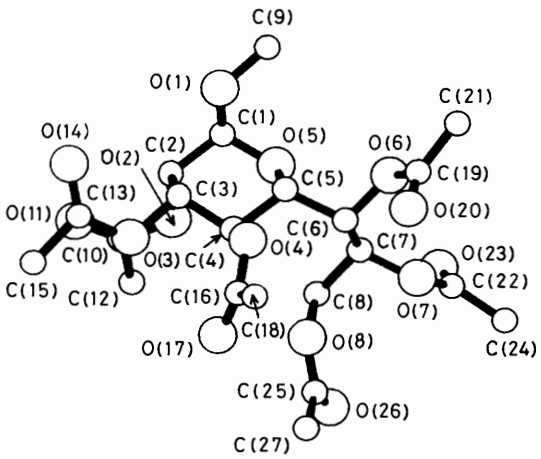
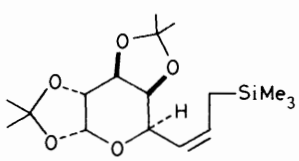
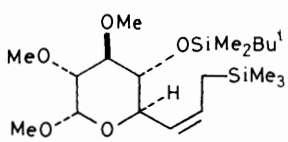


Figure 2. *X*-Ray molecular structure of methyl 2,3,4,6,7,8-hexa-*O*-acetyl-β-L-*threo*-D-*manno*-octopyranoside (**20**)



(22)



(23)

service. ^{13}C N.m.r. spectra were recorded for solutions in [$^2H_6$]dimethyl sulphoxide at 90 MHz by Edinburgh University n.m.r. service; the spectra were referenced to tetramethylsilane by taking the solvent resonance as δ_C 39.6. A Perkin-Elmer Model 141 automatic polarimeter and 1 dm tubes were used for the measurement of specific optical rotations. M.p.s were measured on a Reichert hot-plate apparatus and are uncorrected.

Methyl (E)-2,3,4-*Tri*-O-*benzyl*-6,7-*dideoxy*-α-D-gluco-*oct*-6-*enodialdo*-1,5-*pyranoside* (**7**).—(*a*) A solution of the D-*gluco* aldehyde (**6**) [*ca.* 4.5 g, 9.7 mmol; prepared by Swern oxidation [7] of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside [6] (**5**)] and formylmethylenetriphenylphosphorane [8] (3.3 g, 10.8 mmol) in anhydrous benzene (70 ml) was boiled under reflux for 1.5 h, cooled, and evaporated under diminished pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (50:1) as eluant] gave the *enal* (**7**) (3.57 g, 75%), m.p. 60—60.5 °C (from diethyl ether–hexane); $[\alpha]_D$ +90.5° (*c* 0.9 in $CHCl_3$) [previously reported [17] as a syrup having $[\alpha]_D$ +92° (*c* 2.6 in $CHCl_3$)] (Found: C, 73.55; H, 6.75. $C_{30}H_{32}O_6$ requires C, 73.75; H, 6.6%); δ_H 9.34 (1 H, d, $J_{7,8}$ 8 Hz, CHO), 7.38—7.24 (15 H, 3 × m, 3 × Ph), 6.66 (1 H, dd, $J_{5,6}$ 4.2, $J_{6,7}$ 15.8 Hz, 6-H), 6.28 (1 H, ddd, $J_{5,7}$ 1.7 Hz, 7-H), 4.92 (2 H, ABq, J_{AB} 11 Hz, PhCH_2), 4.73 (2 H, ABq, J_{AB} 12 Hz, PhCH_2), 4.71 (2 H, ABq, J_{AB} 11 Hz, PhCH_2), 4.62 (1 H, d, $J_{1,2}$ 3.6 Hz, 1-H), and 3.35 (3 H, s, OMe).

(*b*) To a solution of the D-glucoside [6] (**5**) (0.446 g, 0.96 mmol) in anhydrous methylene dichloride (20 ml) containing powdered 3 Å molecular sieves [10] (1 g) was added pyridinium chlorochromate [9] (0.41 g, 1.9 mmol), and the mixture was stirred at room temperature for 1.5 h. Formylmethylenetriphenylphosphorane [8] (2.0 g, 6.6 mmol) was then added and stirring was continued for 1 h, whereupon the reaction mixture was poured into diethyl ether. The ethereal solution was filtered and evaporated under diminished pressure. A solution of the residue in chloroform was dried ($MgSO_4$) and concentrated under diminished pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (50:1) as eluant] gave the *enal* (**7**) (0.313 g, 67%), m.p. and mixture m.p. 59—60.5 °C.

Methyl (E)-2,3,4-*Tri*-O-*benzyl*-6,7-*dideoxy*-α-D-gluco-*oct*-6-*enopyranoside* (**8**).—To a stirred and cooled (0 °C) solution of the enal (**7**) (1.9 g, 3.9 mmol) in anhydrous methylene dichloride (10 ml) under nitrogen was gradually added di-isobutylaluminium hydride (1M solution in methylene dichloride; 6 ml, 6 mmol), and the reaction mixture was stirred at 0 °C for 2 h before the excess of the reagent was decomposed with saturated aqueous ammonium chloride solution. More methylene dichloride was then added, inorganic material was filtered off through glass wool, and the filtrate was washed with a little water, dried ($MgSO_4$), and evaporated under diminished pressure. Chromatography of the residue on silica gel

[methylene dichloride–acetone (10:1) as eluant] gave the (E)-*octenopyranoside* (**8**) (1.6 g, 84%), isolated as a syrup that crystallised with time. Trituration with hexane and filtration gave the pure compound (**8**) having m.p. 63.5—64.5 °C; $[\alpha]_D$ + 25° (*c* 1.1 in $CHCl_3$) (Found: C, 73.1; H, 6.8. $C_{30}H_{34}O_6$ requires C, 73.4; H, 7.0%); δ_H 7.38—7.25 (15 H, 3 × m, 3 × Ph), 5.95 and 5.65 (2 H, 2 × m, $J_{6,7}$ 15.5 Hz, 6- and 7-H), 4.90, 4.74, and 4.69 (6 H, 3 × ABq, J_{AB} *ca.* 11 Hz, 3 × PhCH_2), 4.58 (1 H, d, $J_{1,2}$ 3.6 Hz, 1-H), and 3.37 (3 H, s, OMe).

Methyl 6,7,8-*Tri*-O-*acetyl*-2,3,4-*tri*-O-*benzyl*-β-L-threo-D-gluco-*octopyranoside* (**11**).—A solution of the (*E*)-octenopyranoside (**8**) (0.428 g, 0.87 mmol), *N*-methylmorpholine *N*-oxide monohydrate (0.236 g, 1.75 mmol), and osmium tetraoxide (*ca.* 25 mg, *ca.* 0.098 mmol) in acetone–water (8:1; 5 ml) was stirred at room temperature for 18 h and then processed in the usual way.[3] Percolation of the residue in methylene dichloride–acetone (1:1) through a column of silica gel provided a mixture (0.349 g, 76%) of methyl 2,3,4-tri-*O*-benzyl-β-L-*threo*-D-*gluco*-octopyranoside (**9**) [δ_H 3.41 (s, OMe)] and the corresponding α-D-*threo*-D-*gluco* isomer (**10**) [δ_H 3.37 (s, OMe)] in the ratio *ca.* 3:1, respectively.

A solution of the foregoing mixture of triols (**9**) and (**10**) (1.8 g, 3.4 mmol) in anhydrous pyridine (30 ml) and acetic anhydride (20 ml) was kept overnight at room temperature and then poured into ice–water. After conventional extractive work-up, the final residue crystallised from diethyl ether–hexane to give the *triacetate* (**11**) (1.21 g, 54%), m.p. 107.5—108.5 °C (after further recrystallisation); $[\alpha]_D$ + 16° (*c* 1.1 in $CHCl_3$) (Found: C, 66.7; H, 6.65. $C_{36}H_{42}O_{11}$ requires C, 66.4; H, 6.5%); δ_H 7.37—7.25 (15 H, 3 × m, 3 × Ph), 4.89 (2 H, ABq, J_{AB} 10.8 Hz, PhCH_2), 4.85 (2 H, ABq, J_{AB} 10.8 Hz, PhCH_2), 4.70 (2 H, ABq, J_{AB} 12 Hz, PhCH_2), 4.51 (1 H, d, $J_{1,2}$ 3.5 Hz, 1-H), 3.34 (3 H, s, OMe), and 2.01 and 1.98 (9 H, 2 × s, proportions 1:2, 3 × OAc).

Methyl 2,3,4-*Tri*-O-*benzyl*-β-L-threo-D-gluco-*octopyranoside* (**9**).—To a solution of the triacetate (**11**) (1.04 g, 1.6 mmol) in anhydrous methanol (15 ml; warming was necessary to dissolve the solute) was added a small piece of sodium, and the reaction mixture was kept for 3 h at room temperature before being neutralised with Amberlite IR-120(H^+) resin. The resin was filtered off and washed thoroughly with methanol, and the filtrate and the washings were combined and evaporated under diminished pressure. The solid residue was recrystallised from ethyl acetate–hexane to give the *triol* (**9**) (0.755 g, 90%), m.p. 113.5—114.5 °C; $[\alpha]_D$ + 36° (*c* 1 in $CHCl_3$) (Found: C, 68.8; H, 6.6. $C_{30}H_{36}O_8$ requires C, 68.7; H, 6.9%); δ_H 7.57—7.23 (15 H, 3 × m, 3 × Ph), 4.92 (2 H, ABq, J_{AB} 11 Hz, PhCH_2), 4.82 (2 H, ABq, J_{AB} 11 Hz, PhCH_2), 4.71 (2 H, ABq, J_{AB} 12 Hz, PhCH_2), 4.55 (1 H, d, $J_{1,2}$ 3.6 Hz, 1-H), and 3.41 (3 H, s, OMe).

L-threo-L-altro-*Octitol* (**12**).—A solution of the triol (**9**) (2.6 g, 4.96 mmol) in methanol (50 ml) containing 10% Pd/C (2.7 g) was shaken overnight at room temperature under a slight overpressure of hydrogen. The catalyst and the solvent were then removed, and a solution of the product in 1M sulphuric acid (30 ml) was heated for 18 h at 100 °C. After being cooled, the hydrolysate was diluted with water and neutralised with Amberlite IR-45(HO^-) resin, and the resin was filtered off and washed thoroughly with water. The filtrate and the washings were combined and reduced in volume to *ca.* 100 ml, and to a cooled (0 °C) solution containing the octose was gradually added sodium borohydride (1.68 g, *ca.* 44 mmol). The reaction mixture was stirred for 2 h at 0 °C and then overnight at room temperature, before being processed in the usual way[3] to give the crude octitol (**12**) (1.15 g, 96%).

A solution of the octitol (**12**) (1.1 g, 4.5 mmol) in anhydrous pyridine (54 ml) and acetic anhydride (43 ml) was heated for 4.5 h at 100 °C, cooled, and poured into ice–water. Conventional extractive work-up and chromatography of the residue on silica gel [methylene dichloride–acetone (10:1) as eluant] provided L-*threo*-L-*altro*-octitol octa-acetate (**13**) (2.05 g, 78%), $[\alpha]_D$ *ca.* −30° (*c* 1.5 in $CHCl_3$), isolated as a syrup; δ_H(*inter alia*) 2.191, 2.092, 2.045, 2.029, 1.994, 1.984, 1.983, and 1.944 (24 H, 8 × s, 8 × OAc).

Zemplén deacetylation of the octa-acetate (**13**) (0.91 g, 1.57 mmol) in anhydrous methanol (30 ml), essentially as described for the triacetate (**11**), gave the *octitol* (**12**) (0.31 g, 81%), isolated as a syrup that crystallised with time. After recrystallisation from aqueous methanol, it had m.p. 121.5—122.5 °C; $[\alpha]_D$ −2.3° (*c* 1 in H_2O) (Found: C, 39.6; H, 7.3. $C_8H_{18}O_8$ requires C, 39.7; H, 7.5%); δ_C([$^2H_6$]DMSO) 73.89, 73.15, 71.82, 71.27, 70.78, 69.39, 62.96, and 62.59.

Methyl (E)-2,3,4-*Tri*-O-*benzyl*-6,7-*dideoxy*-α-D-manno-*oct*-6-*enodialdo*-1,5-*pyranoside* (**16**).—(*a*) A solution of the D-*manno* aldehyde[13,14] (**15**) (*ca.* 1.4 g, *ca.* 3.0 mmol) and formylmethylenetriphenylphosphorane[8] (1.01 g, 3.3 mmol) in anhydrous benzene (21 ml) was boiled under reflux for 1.5 h, cooled, and evaporated under diminished pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (50:1) as eluant] gave the *enal* (**16**) (0.99 g, 67%), isolated as a pale yellow syrup that was used in the next step without further purification; δ_H 9.44 (1 H, d, $J_{7,8}$ 8 Hz, CHO), 7.39—7.25 (15 H, 3 × m, 3 × Ph), 6.81 (1 H, dd, $J_{5,6}$ 4.3, $J_{6,7}$ 15 Hz, 6-H), 6.42 (1 H, ddd, $J_{5,7}$ 1.7 Hz, 7-H), 4.77 (2 H, ABq, J_{AB} 11 Hz, PhCH_2), 4.75 (3 H, d and ABq, $J_{1,2}$ 1.8, J_{AB} 12.3 Hz, 1-H and PhCH_2), 4.66 (2 H, s, PhCH_2), and 3.31 (3 H, s, OMe).

(*b*) To a solution of the D-mannoside[13] (**14**) (*ca.* 0.3 g, *ca.* 0.65 mmol) in anhydrous methylene dichloride (13.5 ml) containing powdered 3 Å molecular sieves[10] (0.67 g) was added pyridinium chlorochromate[9] (0.275 g, 1.28 mmol), and the mixture was stirred at room temperature for 1.75 h. Formylmethylenetriphenylphosphorane[8] (1.23 g, 4.04 mmol) was then added and stirring was continued for 2.25 h, whereupon the reaction mixture was poured into diethyl ether (70 ml), filtered, and evaporated under diminished pressure. Chromatography of the residue on silica gel [methylene dichloride–acetone (30:1) as eluant] with sacrificial cuts gave the *enal* (**16**) (0.14 g, 44%), $[\alpha]_D$ + 80° (*c* 1.2 in $CHCl_3$) (Found: C, 73.7; H, 6.8. $C_{30}H_{32}O_6$ requires C, 73.75; H, 6.6%). The 360 MHz n.m.r. spectrum of this material was indistinguishable from that of the product obtained in (*a*).

Methyl (E)-2,3,4-*Tri*-O-*benzyl*-6,7-*dideoxy*-α-D-manno-*oct*-6-*enopyranoside* (**17**).—A cooled (0 °C) solution of the enal (**16**) (1.9 g, 3.9 mmol) in anhydrous methylene dichloride (10 ml) under nitrogen was treated with di-isobutylaluminium hydride (1M solution in methylene dichloride; 6 ml, 6 mmol) as described earlier in a similar experiment. Chromatography of the final residue on silica gel [methylene dichloride–acetone (10:1) as eluant] gave the *octenopyranoside* (**17**) (1.49 g, 78%), $[\alpha]_D$ + 45.5° (*c* 0.95 in $CHCl_3$), isolated as a syrup (Found: C, 73.3; H, 7.0. $C_{30}H_{34}O_6$ requires C, 73.4; H, 7.0%); δ_H 7.40—7.25 (15 H, 3 × m, 3 × Ph), 6.02 and 5.81 (2 H, 2 × m, $J_{6,7}$ 15.5 Hz, 6- and 7-H), 4.74 (2 H, ABq, J_{AB} 11 Hz, PhCH_2), 4.76 (2 H, ABq, J_{AB} 12.5 Hz, PhCH_2), 4.70 (1 H, d, $J_{1,2}$ 2 Hz, 1-H), 4.65 (2 H, ABq, J_{AB} 11.9 Hz, PhCH_2), and 3.31 (3 H, s, OMe).

Methyl 2,3,4,6,7,8-*Hexa*-O-*acetyl*-β-L-threo-D-manno-*octopyranoside* (**20**).—A solution of the octenopyranoside (**17**) (1.4 g, 2.85 mmol), *N*-methylmorpholine *N*-oxide monohydrate (0.824 g, 6.1 mmol), and osmium tetraoxide (35 mg, 0.14 mmol) in acetone–water (8:1; 15 ml) was stirred overnight at room temperature and then processed conventionally[3] to give a

Table 1. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for the octose triacetate (**11**)

	x	*y*	*z*
O(1)	303(3)	4 618(4)	2 371(4)
O(2)	−198(3)	3 918(4)	4 168(4)
O(3)	1 316(3)	3 179(4)	4 746(3)
O(4)	2 522(3)	3 521(3)	3 289(4)
O(5)	715(3)	3 251(3)	1 819(3)
O(6)	1 870(3)	3 357(3)	316(3)
O(7)	1 215(3)	1 763(3)	776(4)
O(8)	3 354(3)	1 731(4)	991(4)
O(9)	2 997(4)	4 119(6)	357(6)
O(10)	827(4)	1 274(5)	2 246(5)
O(11)	3 965(4)	1 681(7)	−438(5)
C(1)	186(5)	3 715(6)	2 442(6)
C(2)	290(4)	3 446(6)	3 495(5)
C(3)	1 168(5)	3 586(6)	3 813(5)
C(4)	1 734(4)	3 182(5)	3 099(5)
C(5)	1 538(4)	3 422(5)	2 030(5)
C(6)	2 049(5)	2 988(5)	1 259(6)
C(7)	1 974(5)	2 012(5)	1 190(6)
C(8)	2 607(5)	1 615(6)	493(6)
C(9)	133(6)	4 954(7)	1 415(7)
C(10)	−1 029(4)	3 857(7)	3 973(7)
C(11)	−1 511(5)	4 158(6)	4 855(6)
C(12)	−2 322(5)	4 013(6)	4 836(7)
C(13)	−2 800(6)	4 287(7)	5 648(8)
C(14)	−2 469(7)	4 656(7)	6 441(8)
C(15)	−1 654(7)	4 786(9)	6 443(8)
C(16)	−1 177(6)	4 551(8)	5 642(7)
C(17)	1 231(6)	3 698(7)	5 605(6)
C(18)	1 797(5)	3 354(6)	6 359(6)
C(19)	1 536(7)	2 731(7)	7 021(7)
C(20)	2 072(8)	2 384(8)	7 711(8)
C(21)	2 847(8)	2 645(9)	7 698(8)
C(22)	3 104(7)	3 235(9)	7 048(8)
C(23)	2 576(6)	3 590(8)	6 385(7)
C(24)	3 110(5)	2 907(6)	3 587(7)
C(25)	3 898(5)	3 367(6)	3 584(6)
C(26)	4 446(5)	3 211(7)	4 332(7)
C(27)	5 177(6)	3 631(8)	4 353(8)
C(28)	5 387(6)	4 224(9)	3 680(9)
C(29)	4 833(6)	4 406(8)	2 926(8)
C(30)	4 106(6)	3 974(8)	2 875(7)
C(31)	2 374(6)	3 960(6)	−44(6)
C(32)	2 056(7)	4 415(6)	−912(7)
C(33)	692(6)	1 416(6)	1 385(6)
C(34)	−91(5)	1 234(7)	903(8)
C(35)	4 020(5)	1 742(7)	436(7)
C(36)	4 755(6)	1 877(8)	1 007(9)

Table 2. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for the octose triacetate (**11**)

(a) Bonds

O(1)–C(1)	1.412(11)	C(7)–C(8)	1.542(11)
O(1)–C(9)	1.422(11)	C(10)–C(11)	1.512(12)
O(2)–C(2)	1.422(9)	C(11)–C(12)	1.370(12)
O(2)–C(10)	1.411(9)	C(11)–C(16)	1.346(13)
O(3)–C(3)	1.432(9)	C(12)–C(13)	1.421(15)
O(3)–C(17)	1.419(10)	C(13)–C(14)	1.334(15)
O(4)–C(4)	1.437(9)	C(14)–C(15)	1.372(16)
O(4)–C(24)	1.423(10)	C(15)–C(16)	1.392(15)
O(5)–C(1)	1.414(10)	C(17)–C(18)	1.487(12)
O(5)–C(5)	1.425(9)	C(18)–C(19)	1.385(14)
O(6)–C(6)	1.429(9)	C(18)–C(23)	1.348(13)
O(6)–C(31)	1.345(10)	C(19)–C(20)	1.399(16)
O(7)–C(7)	1.435(9)	C(20)–C(21)	1.352(19)
O(7)–C(33)	1.312(10)	C(21)–C(22)	1.337(18)
O(8)–C(8)	1.425(9)	C(22)–C(23)	1.372(16)
O(8)–C(35)	1.339(11)	C(24)–C(25)	1.493(12)
O(9)–C(31)	1.197(12)	C(25)–C(26)	1.384(12)
O(10)–C(33)	1.206(11)	C(25)–C(30)	1.385(14)
O(11)–C(35)	1.190(12)	C(26)–C(27)	1.380(14)
C(1)–C(2)	1.493(10)	C(27)–C(28)	1.339(17)
C(2)–C(3)	1.539(10)	C(28)–C(29)	1.404(16)
C(3)–C(4)	1.487(10)	C(29)–C(30)	1.384(15)
C(4)–C(5)	1.527(10)	C(31)–C(32)	1.467(13)
C(5)–C(6)	1.505(11)	C(33)–C(34)	1.484(13)
C(6)–C(7)	1.518(12)	C(35)–C(36)	1.463(14)

(b) Angles

C(1)–O(1)–C(9)	113.3(7)	C(12)–C(11)–C(16)	119.7(8)
C(2)–O(2)–C(10)	114.0(6)	C(11)–C(12)–C(13)	119.3(9)
C(3)–O(3)–C(17)	117.1(6)	C(12)–C(13)–C(14)	121.1(9)
C(4)–O(4)–C(24)	115.9(6)	C(13)–C(14)–C(15)	118.3(10)
C(1)–O(5)–C(5)	112.6(6)	C(14)–C(15)–C(16)	121.7(10)
C(6)–O(6)–C(31)	117.9(6)	C(11)–C(16)–C(15)	119.8(9)
C(7)–O(7)–C(33)	116.7(6)	O(3)–C(17)–C(18)	107.2(8)
C(8)–O(8)–C(35)	117.4(7)	C(17)–C(18)–C(19)	119.5(9)
O(1)–C(1)–O(5)	112.0(6)	C(17)–C(18)–C(23)	122.0(9)
O(1)–C(1)–C(2)	108.9(7)	C(19)–C(18)–C(23)	118.3(9)
O(5)–C(1)–C(2)	110.8(7)	C(18)–C(19)–C(20)	119.8(10)
O(2)–C(2)–C(1)	113.6(7)	C(19)–C(20)–C(21)	119.1(11)
O(2)–C(2)–C(3)	107.0(6)	C(20)–C(21)–C(22)	121.2(11)
C(1)–C(2)–C(3)	109.8(6)	C(21)–C(22)–C(23)	119.8(11)
O(3)–C(3)–C(2)	110.5(6)	C(18)–C(23)–C(22)	121.7(10)
O(3)–C(3)–C(4)	106.2(6)	O(4)–C(24)–C(25)	106.6(7)
C(2)–C(3)–C(4)	111.2(6)	C(24)–C(25)–C(26)	119.6(8)
O(4)–C(4)–C(3)	108.1(6)	C(24)–C(25)–C(30)	123.0(8)
O(4)–C(4)–C(5)	106.0(6)	C(26)–C(25)–C(30)	117.3(8)
C(3)–C(4)–C(5)	112.2(6)	C(25)–C(26)–C(27)	120.9(9)
O(5)–C(5)–C(4)	110.5(6)	C(26)–C(27)–C(28)	122.6(10)
O(5)–C(5)–C(6)	108.8(6)	C(27)–C(28)–C(29)	117.4(10)
C(4)–C(5)–C(6)	115.2(6)	C(28)–C(29)–C(30)	120.9(11)
O(6)–C(6)–C(5)	108.8(6)	C(25)–C(30)–C(29)	120.8(9)
O(6)–C(6)–C(7)	108.9(6)	O(6)–C(31)–O(9)	121.3(8)
C(5)–C(6)–C(7)	116.0(7)	O(6)–C(31)–C(32)	113.4(8)
O(7)–C(7)–C(6)	111.4(6)	O(9)–C(31)–C(32)	125.2(9)
O(7)–C(7)–C(8)	105.0(6)	O(7)–C(33)–O(10)	123.8(8)
C(6)–C(7)–C(8)	112.1(7)	O(7)–C(33)–C(34)	112.6(8)
O(8)–C(8)–C(7)	105.0(6)	O(10)–C(33)–C(34)	123.6(9)
O(2)–C(10)–C(11)	110.6(7)	O(8)–C(35)–O(11)	119.5(8)
C(10)–C(11)–C(12)	117.3(8)	O(8)–C(35)–C(36)	113.5(9)
C(10)–C(11)–C(16)	122.9(8)	O(11)–C(35)–C(36)	126.9(9)

mixture (0.96 g, 64%) of methyl 2,3,4-tri-*O*-benzyl-β-L-*threo*-D-*manno*-octopyranoside (**18**) [δ_H 3.35 (s, OMe)] and the corresponding α-D-*threo*-D-*manno* isomer (**19**) [δ_H 3.29 (s, OMe)] in the ratio *ca.* 4:1, respectively.

A solution of the foregoing mixture of triols (**18**) and (**19**) (0.95 g, 1.8 mmol) in methanol (20 ml) containing 10% Pd/C (1 g) was shaken overnight at room temperature under a slight overpressure of hydrogen before being processed in the usual way. A solution of the product in anhydrous pyridine (5 ml) and acetic anhydride (3 ml) was kept for 18 h at room temperature and then poured into ice–water. The precipitate was filtered off and recrystallised from ethanol to give the *hexa-acetate* (**20**) (0.425 g, 46%), m.p. 132—133.5 °C; $[\alpha]_D$ +33° (*c* 1.1 in $CHCl_3$) (Found: C, 49.9; H, 5.9. $C_{21}H_{30}O_{14}$ requires C, 49.8; H, 6.0%); δ_H(*inter alia*) 2.130, 2.056, 2.046, 2.042, 2.038, and 1.958 (18 H, 6 × s, 6 × OAc).

D-erythro-L-altro-*Octitol* (**21**).—To a solution of the hexa-acetate (**20**) (2.6 g, 5.1 mmol) in anhydrous methanol (70 ml; warming was necessary to dissolve the solute) was added a small piece of sodium, and the reaction mixture was kept overnight at room temperature before being processed as described earlier in

Table 3. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for the octose hexa-acetate (**20**)

	x	*y*	*z*
O(1)	1 020(4)	4 545(3)	2 402(2)
O(2)	3 341(4)	2 960(2)	3 343(2)
O(3)	5 853(4)	1 581(3)	5 829(2)
O(4)	1 469(4)	5 592(3)	4 242(2)
O(5)	3 436(4)	4 879(2)	2 839(2)
O(6)	3 974(4)	7 085(2)	3 026(1)
O(7)	6 737(4)	6 700(3)	3 609(2)
O(8)	5 745(4)	5 126(3)	4 396(2)
O(11)	2 196(7)	1 483(4)	3 485(3)
O(14)	3 676(5)	2 094(4)	6 292(2)
O(17)	2 380(6)	4 929(4)	5 116(2)
O(20)	3 022(8)	8 090(4)	3 731(2)
O(23)	8 640(6)	6 178(5)	3 015(3)
O(26)	8 052(8)	4 774(7)	4 710(3)
C(1)	2 367(6)	4 136(4)	2 626(3)
C(2)	1 928(6)	3 415(4)	3 134(2)
C(3)	1 195(6)	4 073(4)	3 642(2)
C(4)	2 311(6)	4 847(4)	3 871(3)
C(5)	2 859(6)	5 494(4)	3 323(2)
C(6)	4 109(6)	6 262(4)	3 470(2)
C(7)	5 770(6)	5 871(4)	3 407(2)
C(8)	6 142(6)	4 938(4)	3 773(2)
C(9)	1 226(8)	5 271(5)	1 912(3)
C(10)	3 365(8)	1 963(5)	3 468(3)
C(12)	4 940(9)	1 585(6)	3 622(4)
C(13)	4 521(8)	2 095(5)	5 851(4)
C(15)	4 238(11)	2 690(6)	5 277(4)
C(16)	1 651(8)	5 572(5)	4 850(3)
C(18)	734(11)	6 383(6)	5 154(3)
C(19)	3 356(7)	7 955(4)	3 212(3)
C(21)	3 133(9)	8 699(5)	2 721(4)
C(22)	8 171(8)	6 754(5)	3 384(3)
C(24)	9 082(9)	7 578(6)	3 668(4)
C(25)	6 768(8)	5 033(6)	4 828(3)
C(27)	6 203(9)	5 316(7)	5 443(3)

a similar experiment. Hydrolysis [1M sulphuric acid (30 ml) for 18 h at 100 °C] of the resulting methyl octopyranoside, and reduction [$NaBH_4$ (1.68 g, *ca.* 44 mmol) in water (100 ml) at 0 °C] of the liberated octose in the usual way [3] furnished the crude product (0.94, 75%), which crystallised on the addition of methanol. Recrystallisation from aqueous methanol gave the *octitol* (**21**), m.p. 144—145 °C; $[\alpha]_D$ *ca.* +1° (*c* 1 in H_2O) (Found: C, 39.9; H, 7.3. $C_8H_{18}O_8$ requires C, 39.7; H, 7.5%); δ_C 71.94, 71.57, 71.51, 71.03, 70.76, 70.49, 64.06, and 63.19.

Crystal-structure Determinations.—(a) *Octose triacetate* (**11**). $C_{36}H_{42}O_{11}$, M = 650.7, orthorhombic, space group $P2_12_12_1$, a = 16.657(13), b = 15.460(16), c = 13.525(10) Å, V = 3 482.9 Å^3, Z = 4, D_c = 1.24 g cm^{-3}, Cu-K_α radiation, λ = 1.5418 Å, μ = 6.74 cm^{-1}.

Data were collected from two crystals (each *ca.* 0.3 × 0.25 × 0.28 mm). Equi-inclination multi-film Weissenberg photographs of reciprocal lattice levels h, k = 0—4, l and hk, l = 0—11 were scanned by using a microdensitometer (S.E.R.C. Service, Daresbury Laboratory); 6 874 measured reflections were merged (SHELX 76) to give the 1 605 unique reflections used in the refinement. No correction was made for absorption.

The structure was solved by direct methods using the SHELX S program system [18] and refined by full-matrix least-squares with anisotropic temperature factors for C and O. Hydrogen atoms were included at calculated positions in the last cycles of refinement using a riding model (C–H = 1.05 Å) with isotropic temperature parameters fixed at U = 0.0700. The final R-factors were R = 0.060 and R' = 0.061. The weighting scheme used was $w = 9.7101/(1 + 0.000\,03F^2)$. The largest features on the final difference map were 0.21, −0.23 e Å^{-3}.

Refinement was carried out on a DEC-10 computer using the SHELX 76 program system [19] with atomic scattering factors taken from the program library. Geometric calculations were performed using XANADU.[20]

Table 4. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for the octose hexa-acetate (**20**)

(a) Bonds

O(1)–C(1)	1.376(7)	O(17)–C(16)	1.207(9)
O(1)–C(9)	1.452(8)	O(20)–C(19)	1.189(8)
O(2)–C(2)	1.438(6)	O(23)–C(22)	1.181(9)
O(2)–C(10)	1.342(7)	O(26)–C(25)	1.193(10)
O(3)–C(13)	1.338(8)	C(1)–C(2)	1.514(8)
O(4)–C(4)	1.469(6)	C(2)–C(3)	1.548(7)
O(4)–C(16)	1.346(7)	C(3)–C(4)	1.492(7)
O(5)–C(1)	1.426(7)	C(4)–C(5)	1.550(7)
O(5)–C(5)	1.428(6)	C(5)–C(6)	1.516(7)
O(6)–C(6)	1.463(6)	C(6)–C(7)	1.535(8)
O(6)–C(19)	1.330(7)	C(7)–C(8)	1.503(8)
O(7)–C(7)	1.446(6)	C(10)–C(12)	1.491(11)
O(7)–C(22)	1.338(8)	C(13)–C(15)	1.504(11)
O(8)–C(8)	1.434(7)	C(16)–C(18)	1.489(11)
O(8)–C(25)	1.304(8)	C(19)–C(21)	1.470(10)
O(11)–C(10)	1.195(9)	C(22)–C(24)	1.481(10)
O(14)–C(13)	1.213(9)	C(25)–C(27)	1.484(11)

(b) Angles

C(1)–O(1)–C(9)	114.7(5)	O(7)–C(7)–C(6)	105.2(4)
C(2)–O(2)–C(10)	119.1(4)	O(7)–C(7)–C(8)	109.3(4)
C(4)–O(4)–C(16)	118.6(4)	C(6)–C(7)–C(8)	115.4(4)
C(1)–O(5)–C(5)	114.0(4)	O(8)–C(8)–C(7)	108.5(4)
C(6)–O(6)–C(19)	117.8(4)	O(2)–C(10)–O(11)	120.8(6)
C(7)–O(7)–C(22)	117.7(4)	O(2)–C(10)–C(12)	112.8(6)
C(8)–O(8)–C(25)	121.1(5)	O(11)–C(10)–C(12)	126.3(6)
O(1)–C(1)–O(5)	113.5(4)	O(3)–C(13)–O(14)	123.3(7)
O(1)–C(1)–C(2)	107.2(4)	O(3)–C(13)–C(15)	112.0(6)
O(5)–C(1)–C(2)	110.6(4)	O(14)–C(13)–C(15)	124.7(7)
O(2)–C(2)–C(1)	106.4(4)	O(4)–C(16)–O(17)	123.7(6)
O(2)–C(2)–C(3)	110.7(4)	O(4)–C(16)–C(18)	111.6(6)
C(1)–C(2)–C(3)	106.4(4)	O(17)–C(16)–C(18)	124.5(6)
C(2)–C(3)–C(4)	111.1(4)	O(6)–C(19)–O(20)	121.5(6)
O(4)–C(4)–C(3)	108.8(4)	O(6)–C(19)–C(21)	113.7(5)
O(4)–C(4)–C(5)	102.4(4)	O(20)–C(19)–C(21)	124.9(6)
C(3)–C(4)–C(5)	108.2(4)	O(7)–C(22)–O(23)	122.5(6)
O(5)–C(5)–C(4)	111.9(4)	O(7)–C(22)–C(24)	112.2(6)
O(5)–C(5)–C(6)	106.7(4)	O(23)–C(22)–C(24)	125.2(7)
C(4)–C(5)–C(6)	114.9(4)	O(8)–C(25)–O(26)	120.2(7)
O(6)–C(6)–C(5)	107.2(4)	O(8)–C(25)–C(27)	114.5(6)
O(6)–C(6)–C(7)	105.4(4)	O(26)–C(25)–C(27)	125.3(7)
C(5)–C(6)–C(7)	115.3(4)		

(b) *Octose hexa-acetate* (**20**). $C_{21}H_{30}O_{14}$, M = 506.45, orthorhombic, space group $P2_12_12_1$, a = 8.662(6), b = 13.175(7), c = 21.957(6) Å, V = 2 505.8 Å^3, Z = 4, D_c = 1.34 g cm^{-3}, graphite-monochromated Cu-K_α radiation, λ = 1.5418 Å, μ = 8.85 cm^{-1}.

A crystal of *ca.* 0.43 × 0.16 × 0.14 mm was mounted on an Enraf-Nonius CAD 4 diffractometer. Intensities for unique data $2 < \theta < 70°$ were measured by an ω—2θ scan and corrected for absorption by a ψ-scan technique using a local program. Out of 2 924 reflections measured, 1 466 reflections with $|F| > 3.0\sigma(F)$ were used in the refinement.

The structure was solved by direct methods using the SHELX S program system [18] and refined as described in (a). Hydrogen atoms were included in the final cycles of refinement using a riding model (C–H = 1.05 Å) with isotropic thermal

parameters refined in groups. The largest features on the final difference map were 0.27, −0.30 e Å^{-3}. The final R-factors were $R = 0.042$ and $R' = 0.046$. The weighting scheme used was $w = 0.0842/(\sigma^2(F) + 0.016\,006F^2)$.

Fractional atomic co-ordinates (corresponding to the absolute configuration), and intramolecular distances and angles are given in Tables 1 and 2 [octose triacetate (**11**)] and Tables 3 and 4 [octose hexa-acetate (**20**)].* In the numbering system used (see Figures 1 and 2), the carbon and oxygen atoms of the parent octose are numbered according to normal carbohydrate nomenclature, while the remaining atoms are numbered arbitrarily.

* *Supplementary data* (see section 5.6.3 of 'Instructions for Authors,' 1988 in the January issue). Tables of structure factors, hydrogen atom co-ordinates, anisotropic thermal parameters, and selected torsion angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank the Commonwealth Scholarship Commission in the United Kingdom for financial support (to A. K. M. S. K.), Dr. I. H. Sadler and his colleagues (Edinburgh University) for recording the ^{1}H and ^{13}C n.m.r. spectra, Dr. D. Watkins and his colleagues (Oxford University) for collecting some of the crystallographic data, and Mr. J. Paton for assistance with the crystal-structure determinations.

References

1 Part 11. J. S. Brimacombe and A. K. M. S. Kabir, *Carbohydr. Res.*, 1988, **179**, 21.
2 Preliminary communication, J. S. Brimacombe and A. K. M. S. Kabir, *Carbohydr. Res.*, 1987, **168**, C5.
3 J. S. Brimacombe, R. Hanna, A. K. M. S. Kabir, F. Bennett, and I. D. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1986, 815.
4 J. K. Cha, W. J. Christ, and Y. Kishi, *Tetrahedron*, 1984, **40**, 2247.
5 J. S. Brimacombe and A. K. M. S. Kabir, *Carbohydr. Res.*, 1986, **150**, 35.
6 H. Hashimoto, K. Asano, F. Fujii, and J. Yoshimura, *Carbohydr. Res.*, 1982, **104**, 87; A. Lipták, I. Jodál, and P. Nánási, *ibid.*, 1975, **44**, 1.
7 K. Omura and D. Swern, *Tetrahedron*, 1978, **34**, 1651; A. J. Mancuso, S.-L. Huang, and D. Swern, *J. Org. Chem.*, 1978, **43**, 2480.
8 S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1961, 1266.
9 E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 1975, 2647.
10 J. Herscovici and K. Antonakis, *J. Chem. Soc., Chem. Commun.*, 1980, 561; J. Herscovici, M.-J. Egron, and K. Antonakis, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1967.
11 D. Horton, A. Liav, and S. E. Walker, *Carbohydr. Res.*, 1973, **28**, 201.
12 V. Van Rheenan, R. C. Kelly, and D. Y. Cha, *Tetrahedron Lett.*, 1976, 1973.
13 H. B. Borén, K. Eklind, P. J. Garegg, B. Lindberg, and A. Pilotti, *Acta Chem. Scand.*, 1972, **26**, 4143.
14 K. Dziewiszek and A. Zamojski, *Carbohydr. Res.*, 1986, **150**, 163 report a similar oxidation.
15 C. S. Hudson, *Adv. Carbohydr. Chem.*, 1945, **1**, 1; J. M. Webber, *ibid.*, 1962, **17**, 15; L. Hough and A. C. Richardson, in 'The Carbohydrates: Chemistry and Biochemistry,' eds. W. Pigman and D. Horton, Academic Press, New York and London, 1972, vol. 1A, p. 113.
16 S. J. Danishefsky, M. P. Deninno, C. B. Phillips, R. E. Zelle, and P. A. Lartey, *Tetrahedron*, 1986, **42**, 2809.
17 S. Jarosz, J. Glodek, and A. Zamojski, *Carbohydr. Res.*, 1987, **163**, 289.
18 G. M. Sheldrick, SHELX S Program for Crystal Structure Determination, University of Göttingen, 1986.
19 G. M. Sheldrick, SHELX 76 Program for Crystal Structure Determination, University of Cambridge, 1975.
20 P. Roberts and G. M. Sheldrick, XANADU Program for Crystallographic Calculations, University of Cambridge, 1975.

Received 9th May 1988; *Paper* 8/08187K