C-Nucleoside Studies. Part III.[1,2] Glycofuranosylethynes from 2,3:5,6-Di-*O*-isopropylidene-D-mannose.

By **J. Grant Buchanan,* Allan D. Dunn,** and **Alan R. Edgar,** Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS

Ethynylmagnesium bromide reacted with 2,3 : 5,6-di-*O*-isopropylidene-D-mannofuranose (2) to give 1,2-dideoxy-4,5 : 7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-oct-1-ynitol (5) (65%), together with the D-*glycero*-D-*galacto*-isomer (3) (5%). The structure of the ethyne (5) was shown by conversion into the ethene (8) which, by ozonolysis, reduction and acidic hydrolysis in sequence, afforded crystalline D-*glycero*-D-*talo*-heptitol (D-volemitol). Oxidation of the ethyne (5) with manganese dioxide afforded crystalline 1,2-dideoxy-4,5 : 7,8-di-*O*-isopropylidene-D-*manno*-oct-1-yn-3-ulofuranose (14b), reduction of which with sodium borohydride gave mainly the diol (3).

Treatment of the ethyne (5) with toluene-*p*-sulphonyl chloride in pyridine yielded 2,3 : 5,6-di-*O*-isopropylidene-β-D-mannofuranosylethyne (16). Treatment of the ethyne (5) with benzoyl chloride followed by methanesulphonyl chloride yielded the 3-*O*-benzoyl-6-*O*-methylsulphonyl compound (21) which, on treatment with sodium methoxide, yielded 2,3 : 5,6-di-*O*-isopropylidene-α-D-talofuranosylethyne (22). Reaction of 1,2-dideoxy-4,5 : 7,8-di-*O*-isopropylidene-D-*glycero*-D-*galacto*-oct-1-ynitol (3) with toluene-*p*-sulphonyl chloride in pyridine yielded 2,3 : 5,6-di-*O*-isopropylidene α-D-mannofuranosylethyne (23). The mannofuranosylethynes (16) and (23) were degraded, by standard procedures, to the lyxofuranosylethynes (18) and (25), respectively.

The glycofuranosylethynes (16) and (23), and (18) and (25) do not obey Hudson's rule. The c.d. of several compounds has been studied.

Treatment of the mannofuranose (2) with ethylmagnesium bromide yields, by contrast, predominantly 7,8-dideoxy-1,2 : 4,5-di-*O*-isopropylidene-L-*glycero*-D-*manno*-octitol (30).

In Part II [1] we described the reaction of 2,3-*O*-isopropylidene-D-ribose with ethynylmagnesium bromide in tetrahydrofuran; the major product, isolated in 70% yield, was the D-*allo*-triol (1). This was a surprising result, since Chilton and his co-workers [3] had reported that the reaction of 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (2) with ethynylmagnesium bromide yielded the D-*glycero*-D-*galacto*-diol (3) as the major product, rather than its 3-epimer (5). In the triol (1), C-3 and C-4 have an *erythro* configuration, whereas in Chilton's case the relationship is *threo*. From molecular models it was not clear to us why there should be such a difference in the two reactions, and we have therefore re-investigated the mannose system. Our conclusion,[2] as reported in detail below, is that the assignment made by Chilton *et al.*[3] is erroneous. We have used the compounds in this series to prepare some new glycofuranosylethynes.

The mannofuranose (2) was treated with ethynylmagnesium bromide in tetrahydrofuran, essentially as described by Chilton,[3] and the crude product acetylated. After preliminary purification by chromatography a crystalline diacetate, m.p. 82.5—83°, was isolated in 53% yield. This compound corresponds to the diacetate, m.p. 80°, isolated by Chilton.[3] Deacetylation of the components of the residual syrup, followed by chromatography, yielded two crystalline isomeric diols, m.p. 75—76° (12%) and 98—98.5° (5%). Deacetylation of the crystalline diacetate yielded the diol of m.p. 75—76°, thus establishing their relationship, in agreement with the original work.[3] The isolated yields corresponding to the two configurations were therefore 65 and 5%.

The crystalline diacetate [(4) or (6)] was treated with lithium aluminium hydride [3,4] to yield the crystalline alkene [(7) or (8)]. The structure of the alkene was

[1] Part II, J. G. Buchanan, A. D. Dunn, and A. R. Edgar, *J.C.S. Perkin I*, 1975, 1191.

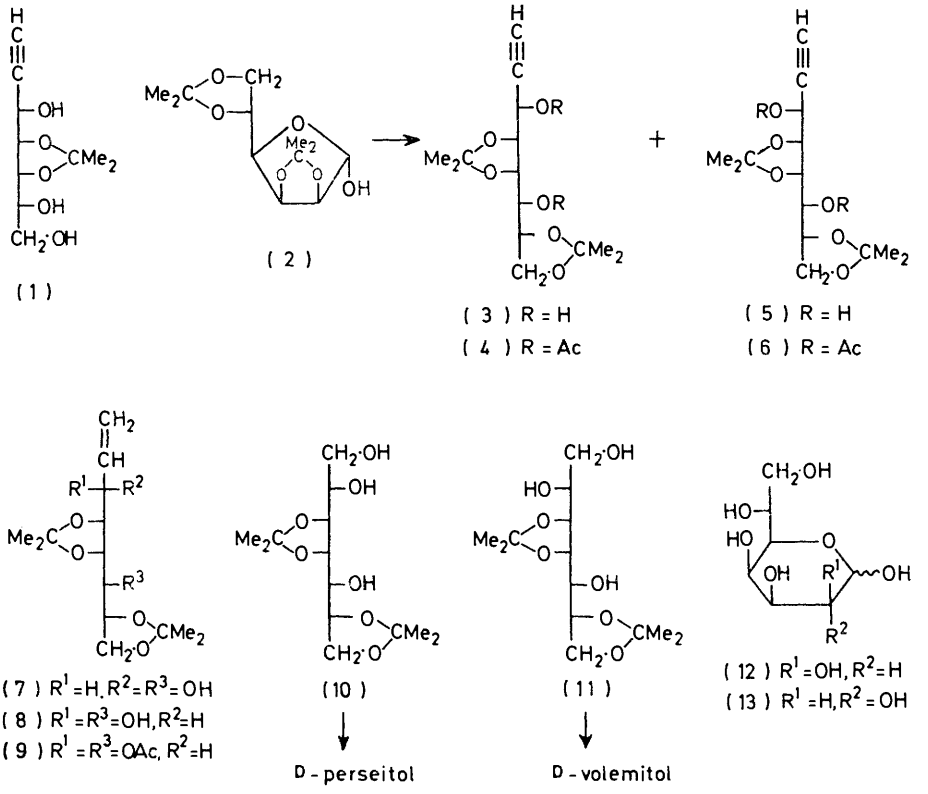
[2] Preliminary communication, J. G. Buchanan, A. D. Dunn, and A. R. Edgar, *Carbohydrate Res.*, 1974, **36**, C5.

[3] W. S. Chilton, W. C. Lontz, R. B. Roy, and C. Yoda, *J. Org. Chem.*, 1971, **36**, 3222.

[4] R. Hems, D. Horton, and M. Nakadate, *Carbohydrate Res.*, 1972, **25**, 205.

proved by ozonolysis, followed by reduction with sodium borohydride. The presumed intermediate triol [(10) or (11)] was not isolated but was subjected to acidic hydrolysis. D-Volemitol (D-*glycero*-D-*talo*-heptitol) [5] was isolated in crystalline form (54% yield). No D-perseitol (D-*glycero*-D-*galacto*-heptitol) was detected. The alkene therefore has the structure (8) and the original diacetate (14b) in 78% yield. When the ketose was reduced with sodium borohydride the diol (3) was by far the major product, as shown by t.l.c. and by the n.m.r. spectrum of the mixture after acetylation. It was isolated after chromatography.

The ring closure of the diol (5) by means of toluene-*p*-sulphonyl chloride in pyridine [1,7] was then studied.

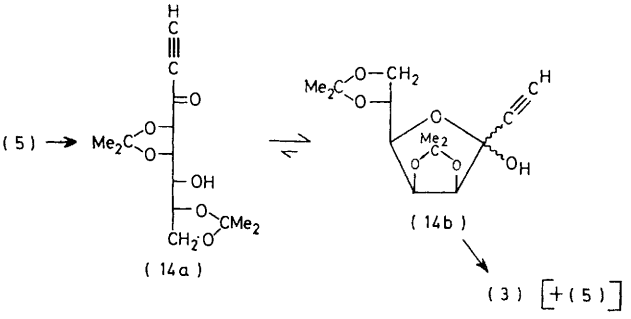


has the D-*glycero*-D-*talo*-structure (6). This result was confirmed by subjecting the alkene (8) to acidic hydrolysis, followed by ozonolysis. D-*glycero*-D-*talo*-Heptose (12)[6] was the only sugar detected by paper chromatography. D-*glycero*-D-*galacto*-Heptose (13),[6] whose R_F value is about half that of the *talo*-isomer, was clearly absent.

The original workers based their structural assignment [3] on the results of ozonolysis of the olefinic diacetate (9) followed by oxidation to the aldonic acid with alkaline silver oxide. The D-*glycero*-D-*galacto*-heptonolactone finally isolated (in 8% yield) may have arisen by base-catalysed epimerisation at C-2 during the oxidation of the heptose derivative.

The D-*glycero*-D-*galacto*-diol (3) is therefore the minor component, m.p. 98—98.5°, of the mixture of diols resulting from the Grignard reaction. It can readily be obtained from the isomeric diol (5) *via* the ketose (14). Oxidation of the diol (5) in benzene solution with manganese dioxide [1] afforded the crystalline ketose

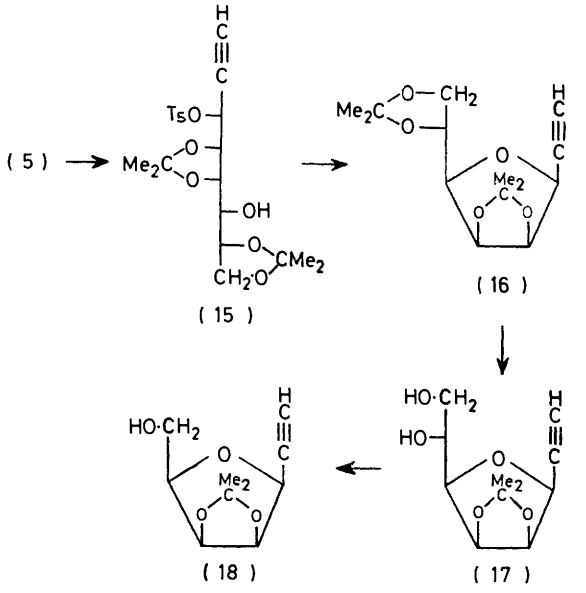
After chromatography on silica gel a crystalline compound, shown to be the β-D-mannofuranosylethyne (16), was isolated in 75% yield.



The *manno*-ethyne (16) would be formed *via* the 3-sulphonate (15). On the other hand sulphonylation of the diol (5) at O-6, followed by ring closure, would lead to the α-D-talofuranosylethyne (22). When the diol (5) was treated with benzoyl chloride (1.06 mol.

[5] W. D. Maclay, R. M. Hann, and C. S. Hudson, *J. Org. Chem.*, 1944, **9**, 293.
[6] H. S. Isbell, *J. Res. Nat. Bur. Stand.*, 1938, **20**, 97.
[7] J. G. Buchanan, A. R. Edgar, and M. J. Power, *J.C.S. Perkin I*, 1974, 1943.

equiv.) in pyridine a crystalline monobenzoate was isolated in about 50% yield. It was shown by n.m.r.



spectroscopy to be the 3-benzoate (19). Subsequent methylsulphonylation yielded the crystalline 6-sulphonate (21), treatment of which with methanolic sodium methoxide gave the crystalline *talo*-ethyne (22), differing from the product of direct cyclisation of the diol (5).

The *manno*-ethyne (16) was converted into the diol (17) by partial acidic hydrolysis. Oxidation of the diol (17) with periodate, followed by reduction with borohydride, afforded the crystalline β-D-lyxofuranosylethyne (18). We have previously described its enantiomer.[1]

When the D-*glycero*-D-*galacto*-diol (3) was treated with toluene-*p*-sulphonyl chloride in pyridine the α-D-mannofuranosylethyne (23), formed *via* the intermediate 3-sulphonate, was isolated in 65% yield after chromatography. Its structure was established by partial acidic hydrolysis to the diol (24), which afforded, upon oxidation with periodate and subsequent reduction with borohydride, α-D-lyxofuranosylethyne (25), identified by comparison with its enantiomer.[1]

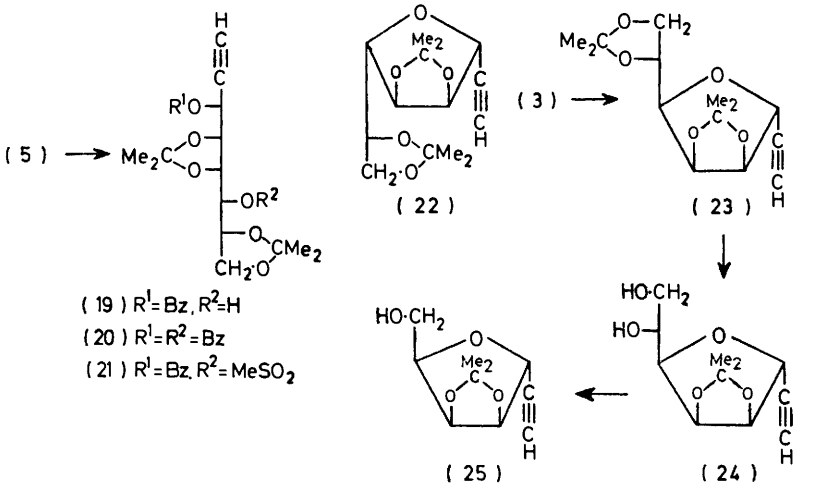
The Table shows that the 2,3-*O*-isopropylideneglycofuranosylethynes do not obey Hudson's rule. For comparison, the ethane derivatives (26) and (27) were prepared by hydrogenation of the corresponding ethynes and they too were found not to obey Hudson's rule. The rotations of the methyl glycosides of 2,3:5,6-di-*O*-isopropylidene-D-mannose are also given in the Table.

Specific rotations of 2,3-*O*-isopropylidene-D-glycofuranosyl derivatives (in $CHCl_3$)

		α	β
(a) Ethynes	*manno* (5,6-*O*-isopropylidene)	−49.4°	+34.6°
	lyxo	−29.1°	+51.3°
	ribo [a]	−48.3°	−21.2° [b]
(b) Ethanes	*manno* (5,6-*O*-isopropylidene)	−28.8°	−15.1°
(c) Methyl glycosides	*manno* [c] (5,6-*O*-isopropylidene)	+50.1°	−58.9°

[a] Ref. 1. [b] G. C. Williams, personal communication. [c] M. H. Randall, *Carbohydrate Res.*, 1969, **11**, 173.

The anomalous behaviour of the ethynes with respect to optical rotations led us to consider the c.d. of these compounds at those short wavelengths in the u.v. where they show absorption. (For the measurements and comments we are indebted to Dr. P. M. Scopes and Professor W. Klyne, Westfield College, London.)

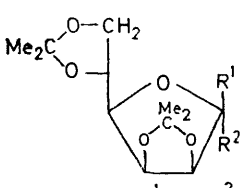


Three ethynes were studied in acetonitrile solution: the β-*lyxo*- and β-*manno*-compounds [(18) and (16)] showed fairly strong positive Cotton effects with a maximum ($\Delta\varepsilon$ *ca.* +2) at about 185 nm; the α-*manno*-compound (23) showed a negative Cotton effect of approximately the same magnitude, although the maximum was not reached.

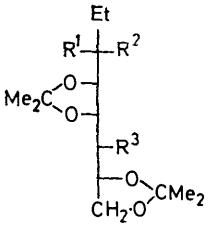
As a control to show that these Cotton effects could be ascribed to the ethyne grouping, one of the corresponding ethanes (27; α-configuration) was studied. This compound showed no significant Cotton effect down to about 190 nm, indicating that the other functional groups (hydroxy and isopropylidenedioxy) are not responsible for the effects observed in the

ethynes. Similarly methyl 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranoside gave no significant Cotton effect.

In a second paper Roy and Chilton [8] have described the reaction of the diacetal (2) with ethylmagnesium bromide in ethereal solution. A deoxyoctitol derivative, supposedly the diol (28), was isolated in 40% yield. Its



(26) R^1 = Et, R^2 = H
(27) R^1 = H, R^2 = Et



(28) R^1 = R^3 = OH, R^2 = H
(29) R^1 = R^3 = OAc, R^2 = H
(30) R^1 = H, R^2 = R^3 = OH
(31) R^1 = H, R^2 = R^3 = OAc
(32) R^1 = R^2 = H, R^3 = OH

structure could be assigned because it differed from the product of catalytic reduction of the major acetylenic carbinol produced by the reaction of the diacetal (2) with ethynylmagnesium bromide. Since we have now shown that the stereochemistry of this acetylenic carbinol is D-*glycero*-D-*talo* (5) and not D-*glycero*-D-*galacto* (3),[3] it follows that the deoxyoctitol derivative isolated from the reaction of the diacetal (2) with ethylmagnesum bromide must be the diol (30) and not the diol (28).

Before re-examining the reaction of the mannofuranose (2) with ethylmagnesium bromide in ether we prepared authentic samples of the ethanes (28) and (30) and their diacetates (29) and (31) by catalytic reduction of the ethynes (5) and (3) followed by acetylation. In our hands the ethane (28) did not crystallise, in contrast to the American work.[8] Hydrogenation of the ethyne (5) also gave some of the propane (32), arising by hydrogenolysis (*cf.* ref. 7).

From the reaction of the mannofuranose (2) with ethylmagnesium bromide in diethyl ether crystalline L-*glycero*-D-*manno*-diol (30) was isolated in 22% yield. After a similar reaction the crude mixture of diols [(30) and (28)] (94%) was acetylated to give the diacetates [(31) and (29)] which were shown by n.m.r. spectroscopy to be in the ratio 63 : 37. When the Grignard reaction was carried out with tetrahydrofuran as solvent the diol (30) was again preferred (70 : 30; 36% isolated). These results show that the stereoselectivities of the reactions of ethynylmagnesium bromide and of ethylmagnesium bromide with the sugar (2) are different.

In the reaction of ethynylmagnesium bromide with 2,3,5-tri-*O*-benzyl-D-ribofuranose [7] the major product (70%) has the D-*threo*-configuration at C-3 and C-4. On the reasonable assumption that reaction occurs with the *aldehydo*-form of the sugar this result is in keeping with Cram's cyclic model for carbonyl compounds containing α-oxygen substituents.[9-11] A similar model accounts for the major product in the reaction of phenylmagnesium bromide wit 2,3-di-*O*-benzyl-D-glyceraldehyde.[12,13] In contrast, when ethynylmagnesium bromide reacts with 2,3,4,5-tetra-*O*-benzoyl-*aldehydo*-L-arabinose (without loss of ester groups) the major product (*ca.* 67%) has the L-*manno*-configuration,[14] but the ester oxygen atom at C-2 in the substrate may be insufficiently nucleophilic to form a cyclic intermediate.

In earlier examples of reactions of 2,3-*O*-isopropylidene-*aldehydo*-sugars with ethynylmagnesium bromide [15,16] and phenylmagnesium bromide,[12,13,17] there was no very strong preponderance of one isomer in the products, but the *threo*-isomer was preferred. One difference between these substrates [2,3-*O*-isopropylidene-D-glyceraldehyde [12,13,16] and 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D [17] (and L) [15]-arabinose] and our own is that there is no large substituent, apart from one of the isopropylidene methyl groups, on the same side of the 1,3-dioxolan ring as the aldehyde group. Although attempts have been made [12,13] to account for some of the stereochemical results, they would not easily explain the differences between the behaviour of ethynylmagnesium bromide and ethylmagnesium bromide noted in this paper. Hough found that allylmagnesium bromide gave mainly the D-*erythro*-isomer on reaction with 2,3-*O*-isopropylideneglyceraldehyde,[18] and Inch has noted differences in the stereoselectivity of phenylmagnesium bromide and methylmagnesium iodide.[19,20] Further work is necessary in this field.

EXPERIMENTAL

The general methods are outlined in Part II.[1]

3,6-*Di*-O-*acetyl*-1,2-*dideoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-glycero-D-talo-*oct*-1-*ynitol* (6).—Ethylmagnesium bromide [from magnesium (3 g) and ethyl bromide (12 ml)] in dry tetrahydrofuran (40 ml) was added dropwise to tetrahydrofuran (40 ml) saturated with acetylene, with constant stirring and with acetylene bubbling into the solution. The addition of acetylene was continued for a further 1 h. 2,3:5,6-Di-*O*-isopropylidene-D-mannofuranose (2) (3 g) was then added in portions, with continuous passage of acetylene. The mixture was stirred for 24 h; t.l.c. then revealed only a trace of the sugar (2). The mixture was treated with aqueous 10% ammonium chloride (5 ml), and filtered through Celite. The precipitate was washed well

[8] R. B. Roy and W. S. Chilton, *J. Org. Chem.*, 1971, **36**, 3242.
[9] D. J. Cram and K. R. Kopecky, *J. Amer. Chem. Soc.*, 1959, **81**, 2748.
[10] D. J. Cram and D. R. Wilson, *J. Amer. Chem. Soc.*, 1963, **85**, 1245.
[11] G. J. Karabatsos, *J. Amer. Chem. Soc.*, 1967, **89**, 1367.
[12] Y. Ohgo, J. Yoshimura, M. Kono, and T. Sato, *Bull. Chem. Soc. Japan*, 1969, **42**, 2957.
[13] J. Yoshimura, Y. Ohgo, K. Ajisaka, and Y. Konda, *Bull. Chem. Soc. Japan*, 1972, **45**, 916.
[14] J. L. Godman, D. Horton, and J. M. J. Tronchet, *Carbohydrate Res.*, 1967, **4**, 392.
[15] D. Horton and J. M. J. Tronchet, *Carbohydrate Res.*, 1966, **2**, 315.
[16] D. Horton, J. B. Hughes, and J. K. Thomson, *J. Org. Chem.*, 1968, **33**, 728.
[17] W. A. Bonner, *J. Amer. Chem. Soc.*, 1951, **73**, 3126.
[18] L. Hough, *J. Chem. Soc.*, 1953, 3066.
[19] T. D. Inch, G. J. Lewis, and N. E. Williams, *Carbohydrate Res.*, 1971, **19**, 17.
[20] T. D. Inch, *Adv. Carbohydrate Chem. Biochem.*, 1972, **27**, 191.

with ethyl acetate and the combined filtrate dried by addition of a large quantity of sodium sulphate. After filtration the solvent was evaporated off to leave a syrup, which was dissolved in dry pyridine (30 ml) and treated with acetic anhydride (15 ml). After 24 h at room temperature, the product was isolated with chloroform, yielding a syrup (4.26 g), which was chromatographed on silica gel (elution with ether). The diacetate (6) crystallised from ether–light petroleum (2.79 g) and was recrystallised from ethanol; yield 2.24 g (53%); m.p. 82.5—83° (lit.,[3] 80°), $[\alpha]_D$ −11.7° (*c* 2.96 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 285 (≡CH), 2 125 (C≡C), 1 760 (C=O), 1 745 (C=O), and 1 380 cm^{-1} (CMe_2); δ (100 MHz; $CDCl_3$) 1.29, 1.34, and 1.48 (12 H, 3s, CMe_2), 2.01 (6 H, s, AcO), 2.32 (1 H, d, $J_{1,3}$ 2 Hz, H-1), 3.60—4.46 (5 H, m), and 5.04—5.26 (2 H, m, H-3, H-6) (Found: C, 58.35; H, 7.1. Calc. for $C_{18}H_{26}O_8$: C, 58.4; H, 7.1%).

1,2-*Dideoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-glycero-D-talo-*oct*-1-*ynitol* (5) *and* 1,2-*Dideoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-glycero-D-galacto-*oct*-1-*ynitol* (3).—The mother liquors left after crystallisation of the diacetate (6) were evaporated to leave a syrup (1.74 g) which was treated with methanolic sodium methoxide (20 ml) [from sodium (140 mg)] at room temperature for 4.5 h. The solvent was evaporated off *in vacuo* and the product isolated with ethyl acetate yielding a syrup (1.14 g), which was chromatographed on silica gel (25 g). Light petroleum–ether (7 : 3) eluted first the D-*glycero*-D-*talo*-ethyne (5), which crystallised from benzene–light petroleum; yield 400 mg (12%); m.p. 75—76° (lit.,[3] 74°), $[\alpha]_D$ −31.6° (*c* 0.67 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 310 (OH), 3 275 (≡CH), 2 120 (C≡C), and 1 390 cm^{-1} (CMe_2); δ (100 MHz; $CDCl_3$) 1.36, 1.41, and 1.53 (12 H, 3s, CMe_2), 2.52 (1 H, d, *J* 2 Hz, ≡CH), 3.04br (1 H, d, OH), and 3.8—4.9 (8 H, m) (Found: C, 58.7; H, 7.8. Calc. for $C_{14}H_{22}O_6$: C, 58.7; H, 7.7%); and was indistinguishable (m.p., mixed m.p., i.r., t.l.c.) from the product of deacetylation of the diacetate (6).

The same solvent then eluted the D-glycero-D-galacto-*ethyne* (3), which crystallised from benzene–light petroleum; yield 155 mg (5%); m.p. 98—98.5°; $[\alpha]_D$ −21.5° (*c* 0.93 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 430 and 3 360 (both OH), 3 280 (≡CH), 2 120 (C≡C), and 1 390 and 1 375 cm^{-1} (both CMe_2); δ (100 MHz; $CDCl_3$) 1.35, 1.41, and 1.54 (12 H, 3s, CMe_2), 2.52 (1 H, d, $J_{1,3}$ 2 Hz, ≡CH), 2.62 (1 H, d, *J* 7 Hz, OH), 2.89 (1 H, d, *J* 5 Hz, OH), and 3.7—4.9 (7 H, m) (Found: C, 58.65; H, 7.7. $C_{14}H_{22}O_6$ requires C, 58.7; H, 7.7%).

3,6-*Di*-O-*acetyl*-1,2-*dideoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-glycero-D-galacto-*oct*-1-*ynitol* (4).—The diol (3) (33 mg) was acetylated with acetic anhydride (200 mg) and pyridine (1 ml). The product was isolated with chloroform to give a syrup (43 mg), purified by distillation (90—100° and 0.02 mmHg); $\nu_{max.}$ (film) 3 270 (≡CH), 2 120 (C≡C), 1 750 (C=O), and 1 380 cm^{-1} (CMe_2); δ (100 MHz; $CDCl_3$) 1.36, 1.38, 1.41, and 1.52 (12 H, 4s, CMe_2), 2.15 (6 H, s, AcO), 2.53 (1 H, d, $J_{1,3}$ 2 Hz, H-1), 3.76—4.56 (5 H, m), 5.28 (1 H, m, H-6), and 5.54 (1 H, m, H-3); *m/e* 355 (*M* − 15).

1,2-*Dideoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-glycero-D-talo-*oct*-1-*enitol* (8).—The ethyne (6) (753 mg) in dry tetrahydrofuran (25 ml) was heated under reflux with lithium aluminium hydride (720 mg) for 21 h. The mixture was cooled in ice and the excess of reagent destroyed by cautious addition of aqueous 10% ammonium chloride (5 ml). The mixture was filtered through Celite and the residue washed with ethyl acetate. The filtrate and washings were dried (Na_2SO_4) and evaporated *in vacuo* yielding the crude ethene (8) as a syrup which was chromatographed on silica gel (15 g). Light petroleum–ether (7 : 3) eluted the pure ethene (8) (490 mg, 83%), which slowly crystallised as needles. Recrystallised from ether–light petroleum the *ethene* (8) had m.p. 45—46°, $[\alpha]_D$ +0.90° (*c* 1.10 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 100 and 3 040 (both =CH_2), 1 600 (C=C), and 1 390 and 1 380 cm^{-1} (both CMe_2); δ (100 MHz; $CDCl_3$) 1.34, 1.39, 1.42, and 1.51 (12 H, 4s, CMe_2), 3.08br (2 H, s, exchangeable with D_2O, OH), 3.8—4.7 (7 H, m), 5.35 (2 H, m, =CH_2), and 6.00 (1 H, ddd, =CH) (Found: C, 58.6; H, 8.5. $C_{14}H_{24}O_6$ requires C, 58.3; H, 8.3%).

D-glycero-D-talo-*Heptitol* (D-*Volemitol*).—The ethene (8) (220 mg) was dissolved in ethanol (40 ml), the solution was cooled to −70 °C, and ozonised oxygen was bubbled through for 1 h. The solution was evaporated to half bulk *in vacuo*, water (5 ml) and sodium borohydride (200 mg) were added, and the solution was kept at room temperature for 90 min. It was then passed through a column of Amberlite IR 120 (H^+) resin (20 ml) (elution with 50% aqueous methanol). The eluate was evaporated *in vacuo* yielding a syrup, from which methanol was evaporated to remove borate. The resulting syrup in methanol (20 ml) was then heated under reflux with Amberlite IR 120 (H^+) resin (250 mg) for 2 h, and then passed through a column of Amberlite MB 3 resin (10 ml). Evaporation of the eluate *in vacuo* yielded a pale yellow syrup (140 mg), shown by paper chromatography to contain volemitol and a little mannitol, but no perseitol. The alditols were detected by alkaline silver nitrate.[21] Crystallisation from methanol yielded D-volemitol (89 mg, 54%), m.p. 150.5—152°. Recrystallised from aqueous methanol (to remove a trace of mannitol) it had m.p. 152—153°, and was identical (mixed m.p. and i.r. spectrum) with authentic D-volemitol.[5]

Degradation of 1,2-*Dideoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-glycero-D-talo-*oct*-1-*enitol* (8) *to a Heptose*.—The ethene (8) (50 mg), dissolved in 70% acetic acid (5 ml), was heated at 100 °C for 1 h. The mixture was evaporated to dryness and the resulting syrup dissolved in ethanol (10 ml). The solution was cooled in ice and ozonised oxygen was bubbled through for 15 min. Water was added and the solvent removed *in vacuo* to leave a syrup (21 mg) which was examined by paper chromatography. Only D-*glycero*-D-*talo*-heptose (12) was detected by the aniline phthalate spray [comparison with authentic D-*glycero*-D-*talo*-*heptose* [6] and D-*glycero*-D-*galacto*-heptose (13) [6]]. The ratio of R_F values of heptoses (13) and (12) was 0.47.

1,2-*Dideoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-manno-*oct*-1-*yn*-3-*ulofuranose* (14).—The diol (5) (180 mg), dissolved in benzene (25 ml), was stirred with active manganese dioxide [1] (2.5 g) for 20 min at room temperature. The solution was filtered and evaporated *in vacuo* to yield a thick syrup (171 mg) which slowly crystallised. Recrystallisation from benzene–light petroleum yielded the pure *ketose* (14b) (140 mg, 78%), m.p. 126—128°, $[\alpha]_D$ −42.8° (*c* 0.63 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 305 (OH), 3 285 (≡CH), 2 125 (C≡C), and 1 385, 1 380sh, and 1 370 cm^{-1} (all CMe_2); δ (100 MHz; $CDCl_3$) 1.39, 1.47, and 1.54 (12 H, 3s, CMe_2), 2.74 (1 H, s, ≡CH), 3.88 (1 H, s, exchangeable in D_2O, HO-3), and 3.92—5.0 (6 H, m) (Found: C, 59.3; H, 7.0. $C_{14}H_{20}O_6$ requires C, 59.2; H, 7.0%).

Reduction of the Ketose (14) *with Sodium Borohydride*.—The sugar (14) (68 mg) was dissolved in 20% aqueous ethanol (6 ml) and sodium borohydride (50 mg) was added.

[21] W. E. Trevelyan, D. P. Procter, and J. S. Harrison, *Nature*, 1950, **166**, 444.

After 2.5 h at room temperature the product was isolated, with chloroform, as a syrup (50 mg). T.l.c. showed the presence of the ethynes (3) (by far the major product) and (5). The syrup (50 mg) was acetylated with acetic anhydride (100 mg) and pyridine (1 ml) and the product isolated, with chloroform, as a pale yellow syrup (60 mg). The n.m.r. spectrum (100 MHz, CCl_4) showed the presence of the diacetates (4) (major product) and (6), but it was not possible to measure the ratio of the two.

A proportion of the diacetate mixture (50 mg) was deacetylated with methanolic sodium methoxide [10 ml; from sodium (5 mg)]. The resulting diols [(3) and (5)] were chromatographed on silica gel (3 g). Light petroleum–ether (7 : 3) eluted the pure *galacto*-diol (24 mg), which crystallised from ether–light petroleum; m.p. 97.5—98°; identical (i.r., t.l.c., mixed m.p.) with the diol (3) described above.

2,3:5,6-*Di*-O-*isopropylidene*-β-D-*mannofuranosylethyne* (16).—The diol (5) (500 mg), in dry pyridine (10 ml), was treated with toluene-*p*-sulphonyl chloride (1.5 g) at 100 °C for 6 h. The excess of acid chloride was destroyed with water, the solution was evaporated *in vacuo*, and pyridine was removed by evaporation of ethanol from the residue. The syrupy product was chromatographed on silica gel (5 g). Light petroleum–ether (1 : 1) eluted the ethyne (16), which crystallised from ether–light petroleum; yield 266 mg (57%); m.p. 117—118°. Sublimation yielded the pure *ethyne* (16), m.p. 120° (higher than that quoted in ref. 2), $[\alpha]_D$ +34.6° (*c* 0.84 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 260 (≡CH), 2 130 (C≡C), and 1 395sh, 1 390, and 1 385 cm^{-1} (all CMe_2); δ (100 MHz; $CDCl_3$) 1.36, 1.42, and 1.55 (12 H, 3s, CMe_2), 2.58 (1 H, d, *J* 2 Hz, ≡CH), 3.44 (1 H, dd), and 3.8—5.0 (6 H, m) (Found: C, 62.6; H, 7.5. $C_{14}H_{20}O_5$ requires C, 62.3; H, 7.5%). Rechromatography of material left on evaporation of the mother liquors, on silica gel, yielded further ethyne (16) (85 mg, 75% in all).

Benzoylation of 1,2-*Dideoxy*-4,5:7,8-*di*-O-*isopropylidene*-D-glycero-D-talo-*oct*-1-*ynitol* (5).—The ethyne (5) (0.50 g) in dry pyridine (2 ml) was treated with benzoyl chloride (260 mg, 1.06 mol. equiv.) at room temperature for 66 h. T.l.c. indicated the presence of three products. Isolation with chloroform yielded a syrup (685 mg), which was chromatographed on silica gel (12 g). Light petroleum–ether (7 : 3) eluted first the *dibenzoate* (20) (109 mg, 13%), m.p. 168—169° (from ethanol), $[\alpha]_D$ −79° (*c* 0.71 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 255 (≡CH), 2 125 (C≡C), 1 735 (C=O), and 1 395, 1 385, and 1 380 cm^{-1} (all CMe_2); δ (100 MHz; $CDCl_3$) 1.23, 1.30, 1.45, and 1.62 (12 H, 4s, CMe_2), 2.45 (1 H, d, *J* 2 Hz, ≡CH), 3.9—4.8 (5 H, m), 5.5—5.7 (2 H, m, H-3, H-6), 7.2—7.7 (6 H, m), and 7.90—8.20 (4 H, m) (Found: C, 68.0; H, 6.0. $C_{28}H_{30}O_8$ requires C, 68.0; H, 6.1%). Light petroleum–ether (7 : 3) next eluted the monobenzoate (19) (381 mg), slightly contaminated with the dibenzoate (20), m.p. 102—103° (from ether–light petroleum). Repetition of the chromatography yielded the pure *monobenzoate* (19) (326 mg, 47%), m.p. 106.5—107°, $[\alpha]_D$ −29.1° (*c* 0.275 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 540 (OH), 3 260 (≡CH), 2 125 (C≡C), 1 740 (C=O), and 1 395, 1 385, and 1 375sh cm^{-1} (all CMe_2); δ (100 MHz; $CDCl_3$) 1.28, 1.31, 1.46, and 1.58 (12 H, 4s, CMe_2), 2.25 (1 H, d, *J* 8 Hz, exchangeable with D_2O, OH), 2.55 (1 H, d, $J_{1,3}$ 2 Hz, ≡CH), 3.6—4.2 (4 H, m), 4.4—4.7 (2 H, m), 5.90 [1 H, dd, $J_{1,3}$ 2, $J_{3,4}$ 6 Hz, H-3 (proved by decoupling experiments)], 7.2—7.7 (3 H, m), 7.9—8.1 (2 H, m) (Found: C, 64.6; H, 6.5. $C_{21}H_{26}O_7$ requires C, 64.6; H, 6.7%).

Elution with ethyl acetate yielded a syrup (173 mg, 25%), which slowly crystallised, m.p. 113—117°. The product, which was not further characterised, was believed to be the 6-monobenzoate.

3-O-*Benzoyl*-1,2-*dideoxy*-4,5:7,8-*di*-O-*isopropylidene*-6-O-*methylsulphonyl*-D-glycero-D-talo-*oct*-1-*ynitol* (21).—The monobenzoate (19) (118 mg) in dry pyridine (1 ml) was treated with methanesulphonyl chloride (200 mg) for 24 h at room temperature. Isolation with chloroform yielded a syrup (135 mg), which was chromatographed on silica gel (8 g). Light petroleum–ether (7 : 3) eluted the methanesulphonate (21) (130 mg), which crystallised from ethanol; yield 115 mg (72%); m.p. 126—127°. Recrystallised from aqueous ethanol it had m.p. 132—133°, $\nu_{max.}$ (KBr) 3 250 (≡CH), 2 125 (C≡C), 1 725 (C=O), 1 600 (Ph), 1 390 and 1 380 (both CMe_2), 1 170 (SO_2), and 710 cm^{-1} (Ph); δ (100 MHz; $CDCl_3$) 1.29, 1.42, 1.44, and 1.62 (12 H, 4s, CMe_2), 2.58 (1 H, d, *J* 2 Hz, ≡CH), 3.11 (3 H, s, SO_2Me), 3.9—4.7 (5 H, m), 5.13 (1 H, complex t, H-6), 5.98 (1 H, complex q, $J_{3,4}$ 2.5 Hz, H-3), 7.2—7.7 (3 H, m), and 8.0—8.2 (2 H, m); *m/e* 453 (*M* − 15).

2,3:5,6-*Di*-O-*isopropylidene*-α-D-*talofuranosylethyne* (22).—The sulphonate (21) (150 mg) was treated with sodium methoxide [from sodium (30 mg)] in methanol (30 ml) at room temperature. T.l.c. indicated that no mesylate remained after 15 min. Isolation with chloroform yielded a syrup which was chromatographed on silica gel (10 g). Light petroleum–ether (3 : 1) eluted the pure *ethyne* (22) (73 mg, 71%), which crystallised. After vacuum sublimation (90—100° and 0.02 mmHg) it had m.p. 68—69°, $[\alpha]_D$ +2.6° (*c* 0.76 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 260 (≡CH), 2 115 (C≡C), and 1 390 and 1 375 cm^{-1} (both CMe_2); δ (100 MHz; $CDCl_3$) 1.35, 1.38, 1.47, and 1.54 (12 H, 4s, CMe_2), 2.54 (1 H, d, *J* 2 Hz, ≡CH), and 3.7—4.9 (7 H, m) (Found: C, 62.5; H, 7.3. $C_{14}H_{20}O_5$ requires C, 62.7; H, 7.5%).

2,3-O-*Isopropylidene*-β-D-*mannofuranosylethyne* (17).—The ethyne (16) (220 mg) in 80% acetic acid (3 ml) was heated at 56 °C for 20 min. Evaporation *in vacuo* yielded a syrup, which was chromatographed on silica gel (10 g). Ether eluted the *ethyne* (17) (142 mg, 76%), which crystallised; m.p. 92° (from ether–light petroleum), $[\alpha]_D$ +34.8° (*c* 0.46 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 420 (OH), 3 250 (≡CH), 2 130 (C≡C), and 1 390 cm^{-1} (CMe_2); δ (100 MHz; $CDCl_3$) 1.38 (3 H, s, CMe_2), 1.54 (3 H, s, CMe_2), 2.57 (1 H, d, *J* 2 Hz, ≡CH), 2.77 (1 H, s, exchangeable in D_2O, OH), 3.24 (1 H, s, exchangeable in D_2O, OH), and 3.4—4.9 (7 H, m) (Found: C, 57.8; H, 7.2. $C_{11}H_{16}O_5$ requires C, 57.9; H, 7.0%).

2,3-O-*Isopropylidene*-β-D-*lyxofuranosylethyne* (8).—The ethyne (17) (110 mg) in ethanol (1 ml) was treated with a solution of sodium periodate (250 mg) in water (5 ml) for 1 h at room temperature. Ethanol (100 ml) was then added and the solution filtered and evaporated *in vacuo*. The syrupy product (90 mg), isolated with chloroform, was dissolved in ethanol (5 ml) and sodium borohydride (150 mg) in water (1 ml) was added. After 2 h at room temperature the product was isolated with chloroform, yielding a crystalline residue (81 mg, 85%), m.p. 100°, on evaporation. Recrystallisation from benzene–light petroleum yielded the lyxo-*ethyne* (18) as needles (73 mg, 75%), m.p. 106°. Vacuum sublimation (100—110° and 0.2 mmHg) raised the m.p. to 108—108.5°; $[\alpha]_D$ +51.3° (*c* 0.605 in $CHCl_3$) (the specific rotation given in ref. 2 is incorrect); $\nu_{max.}$ (KBr) 3 530 (OH), 3 240 (≡CH), 2 130 (C≡C), and 1 390 and 1 380 cm^{-1} (both CMe_2); δ (100 MHz; $CDCl_3$) 1.34 and 1.54 (6 H, 2s, CMe_2), 2.08 (1 H, t, *J* 6 Hz,

exchangeable in D_2O, OH), 2.59 (1 H, d, *J* 2 Hz, ≡CH), 3.66 (1 H, m), 3.92 [2 H, m, H-5 and -5′ (decoupled by D_2O exchange)], 4.24 (1 H, m), and 4.74 (2 H, m); *m/e* 183 (*M* − 15) (Found: C, 60.6; H, 7.0. $C_{10}H_{14}O_4$ requires C, 60.6; H, 7.1%).

2,3:5,6-*Di*-O-*isopropylidene*-α-D-*mannofuranosylethyne* (23).—The diol (3) (200 mg) in dry pyridine (5 ml) was treated with toluene-*p*-sulphonyl chloride (400 mg) at 80—90 °C for 4 h. T.l.c. indicated that no starting material remained. The product was isolated with chloroform, yielding a syrup (173 mg) which was chromatographed on silica gel (12 g). Light petroleum–ether (7 : 3) eluted the *ethyne* (23) (121 mg, 65%), which crystallised and was purified by vacuum sublimation (95—100° and 0.02 mmHg); m.p. 77°, $[\alpha]_D$ −49.4° (*c* 0.87 in $CHCl_3$); $\nu_{max.}$ (KBr) 3 275 (≡CH), 2 110 (C≡C), and 1 395, 1 380, and 1 375 cm^{-1} (all CMe_2); δ (100 MHz; $CDCl_3$) 1.37, 1.40, 1.48, and 1.50 (12 H, 4s, CMe_2), 2.47 (1 H, d, *J* 2 Hz, ≡CH), and 3.8—5.0 7 H, m) (Found: C, 62.6; H, 7.4. $C_{14}H_{20}O_5$ requires C, 62.7; H, 7.5%).

2,3-O-*Isopropylidene*-α-D-*mannofuranosylethyne* (24).—The ethyne (23) (65 mg) dissolved in 80% acetic acid (1 ml) was heated at 50—55 °C for 25 min. The solution was evaporated *in vacuo* yielding a syrup, which was chromatographed on silica gel (3 g). Light petroleum–ether (3 : 2) and also ether eluted the ethyne (24) (44 mg, 80%), which crystallised from ether–light petroleum; m.p. 70°; $\nu_{max.}$ (KBr) 3 360 and 3 300 (both OH), 3 280 (≡CH), 2 110 (C≡C), and 1 385 and 1 375 cm^{-1} (both CMe_2); *m/e* 213 (*M* − 15).

2,3-O-*Isopropylidene*-α-D-*lyxofuranosylethyne* (25).—The *manno*-ethyne (24) was dissolved in water (2 ml) containing 2 drops of ethanol and sodium periodate (50 mg) was added. After 1 h at room temperature the solution was diluted with ethanol (40 ml) and filtered. The filtrate was evaporated *in vacuo* and the residue dissolved in 50% aqueous ethanol (2 ml). Sodium borohydride (75 mg) was added and after 90 min the solvent was evaporated off *in vacuo* and the product isolated with chloroform. The resulting syrup was chromatographed on silica gel (3 g). Light petroleum–ether (7 : 3) eluted the crystalline *ethyne* (25) (21 mg, 71%), which was purified by vacuum sublimation (80—90° and 0.05 mmHg); m.p. 60—61°, $[\alpha]_D$ −29.1° (*c* 0.79 in $CHCl_3$). The i.r. spectrum was identical with that of the L-isomer,[1] m.p. 60.5—61°; $[\alpha]_D$ +25.1° ($CHCl_3$).

2,3:5,6-*Di*-O-*isopropylidene*-β-D-*mannofuranosylethane* (26).—The ethyne (16) (75 mg) in ethanol (25 ml) was hydrogenated at room temperature and 1 atm over 10% palladium–charcoal (50 mg). The mixture was filtered and evaporated *in vacuo* to yield a syrup which was chromatographed on silica gel (3 g). Ether eluted the *ethane* (26) as a syrup (65 mg, 85%), which was purified by sublimation (85—95° and 0.05 mmHg); $[\alpha]_D$ −15.1° (*c* 1.16 in $CHCl_3$); $\nu_{max.}$ (film) 1 375 and 1 365 cm^{-1} (both CMe_2); δ (100 MHz; $CDCl_3$) 0.90—1.90 (17 H, m, CMe_2, $CH_2{\cdot}CH_3$), 3.2—3.6 (2 H, m), and 3.9—4.8 (5 H, m); *m/e* 257 (*M* − 15) (Found: C, 61.6; H, 8.9. $C_{14}H_{24}O_5$ requires C, 61.8; H, 8.8%).

2,3:5,6-*Di*-O-*isopropylidene*-α-D-*mannofuranosylethane* (27).—The ethyne (23) (35 mg) in ethanol (30 ml) was hydrogenated at room temperature and 1 atm over 10% palladium–charcoal (20 mg) until t.l.c. in light petroleum–ether (1 : 1) indicated that no ethyne (23) remained. The mixture was then filtered through Celite, and the filtrate evaporated *in vacuo* yielding a syrup, which was chromatographed on silica gel (3 g). Ether eluted the ethane (27) (30 mg, 85%) as a syrup, which was purified by sublimation *in vacuo* (85—90° and 0.05 mmHg). The pure ethane (27) had $[\alpha]_D$ −28.8° (*c* 1.04 in $CHCl_3$); $\nu_{max.}$ (film) 1 380 and 1 375 cm^{-1} (both CMe_2); δ (100 MHz; $CDCl_3$) 0.90—1.95 (17 H, m, CMe_2, $CH_2{\cdot}CH_3$) and 3.6—4.9 (7 H, m); *m/e* 257 (*M* − 15) (Found: C, 62.05; H, 9.0. $C_{14}H_{24}O_5$ requires C, 61.8; H, 8.8%).

7,8-*Dideoxy*-1,2:4,5-*di*-O-*isopropylidene*-D-glycero-D-manno-*octitol* (28).—The ethyne (5) (400 mg) in ethanol (30 ml) was hydrogenated at room temperature and 1 atm over 10% palladium–charcoal (400 mg). The mixture was filtered and evaporated to yield a syrup (391 mg). T.l.c. indicated the presence of two components, neither of which decolourised permanganate. The syrup was chromatographed on silica gel (12 g). Light petroleum–ether (4 : 1) eluted the n-propyl derivative (32) (30 mg, 8%) as a syrup, which crystallised. Vacuum sublimation (100—110° and 0.01 mmHg) yielded the pure propane (32), m.p. 95—96°; *m/e* 274 (M^+) and 273 (*M* − 1).

Light petroleum–ether (7 : 3) eluted the *diol* (28) as a syrup (297 mg, 73%), which was purified by vacuum sublimation (90—110° and 0.01 mmHg); $[\alpha]_D$ −31.2° (*c* 0.32 in $CHCl_3$); $\nu_{max.}$ (film) 3 440 (OH) and 1 385 and 1 375 cm^{-1} (both CMe_2); δ (100 MHz; $CDCl_3$) 0.98 (3 H, t, Me), 1.1—2.0 (14 H, m, CH_2, $2CMe_2$), 2.58 (1 H, d, *J* 4 Hz, exchangeable with D_2O, OH), 3.7—4.2 (6 H, m), and 4.34 (1 H, d) (Found: C, 57.9; H, 9.2. $C_{14}H_{26}O_6$ requires C, 57.9; H, 9.0%).

3,6-*Di*-O-*acetyl*-7,8-*dideoxy*-1,2:4,5-*di*-O-*isopropylidene*-D-glycero-D-manno-*octitol* (29).—The diol (28) (80 mg) was dissolved in dry pyridine (1 ml) and acetic anhydride (0.500 g) was added. After 72 h at room temperature the product was isolated with chloroform yielding the diacetate (29) as a syrup (101 mg, 98%). Vacuum sublimation (90—110° and 0.01 mmHg) gave the pure *diacetate* (29), $[\alpha]_D$ −16.7° (*c* 0.30 in $CHCl_3$); $\nu_{max.}$ (film) 1 750 (C=O) and 1 380sh and 1 370 cm^{-1} (both CMe_2); δ (100 MHz; $CDCl_3$) 0.89 (3 H, t, Me), 1.1—2.0 (14 H, m, CMe_2, CH_2), 2.05 and 2.08 (6 H, 2s, COMe), 3.8—4.5 (5 H, m), 4.6—4.8 (1 H, m, H-3), and 5.1—5.2 (1 H, m, H-6); *m/e* 359 (*M* − 15) (Found: C, 57.6; H, 8.0. $C_{18}H_{30}O_8$ requires C, 57.7; H, 8.1%).

7,8-*Dideoxy*-1,2:4,5-*di*-O-*isopropylidene*-L-glycero-D-manno-*octitol* (30).—The ethyne (3) (80 mg) in ethanol (10 ml) was hydrogenated at room temperature and 1 atm over 10% palladium–charcoal (100 mg). The mixture was filtered and evaporated to yield a syrup (70 mg). T.l.c. indicated the presence of two compounds, both unreactive to permanganate, the major component having the same R_F value as (3). The syrupy product was chromatographed on silica gel (8 g). Light petroleum–ether (4 : 1) eluted the diol (30) (60 mg, 74%), which crystallised. Recrystallisation from benzene–light petroleum *needles* (46 mg, 57%), m.p. 85—85.5°, $[\alpha]_D$ −13.5° (*c* 2.05 in $CHCl_3$) {lit.,[8] m.p. 78°, $[\alpha]_D$ −17.7° (MeOH)}; $\nu_{max.}$ (KBr) 3 200 (OH) and 1 380 and 1 370 cm^{-1} (both CMe_2); δ [100 MHz; $(CD_3)_2SO$] 0.92 (3 H, t, Me), 1.0—1.8 (14 H, m, CMe_2, CH_2), 3.36—4.20 (7 H, m), and 5.12 (2 H, q) (Found: C, 57.7; H, 9.0. $C_{14}H_{26}O_6$ requires C, 57.9; H, 9.0%).

3,6-*Di*-O-*acetyl*-7,8-*dideoxy*-1,2:4,5-*di*-O-*isopropylidene*-L-glycero-D-manno-*octitol* (31).—The diol (30) (100 mg) in dry pyridine (4 ml) was treated with acetic anhydride (300 mg) at room temperature for 18 h. Isolation with chloroform yielded a syrup (126 mg, 98%), which was purified by

vacuum sublimation (90—100° and 0.1—0.02 mmHg) to yield the pure *diacetate* (31), $[\alpha]_D$ −19.7° (*c* 0.305 in $CHCl_3$); $\nu_{max.}$ (film) 1 745 (C=O), 1 380sh, and 1 370 cm^{-1} (both CMe_2); δ (100 MHz; $CDCl_3$) 0.90 (3 H, t, Me), 1.3—1.8 (14 H, m, CH_2 and CMe_2), 2.08 (3 H, s, COMe), 2.14 (3 H, s, COMe), 3.7—4.4 (5 H, m), and 4.8—5.1 (2 H, m, H-3, H-6) (Found: C, 57.4; H, 7.8. $C_{18}H_{30}O_8$ requires C, 57.7; H, 8.1%).

Reaction of 2,3:5,6-*Di*-O-*isopropylidene*-D-*mannofuranose* (2) *with Ethylmagnesium Bromide.*—(a) *In ether.* A slurry of the sugar (2) (3 g) in dry ether (25 ml) was added to ethylmagnesium bromide [from magnesium (3 g) and ethyl bromide (10.5 ml)] in dry ether (60 ml) under nitrogen. After 7 min t.l.c. indicated that no sugar (2) remained. After 1 h wet ether (200 ml) was added and the mixture was then treated with aqueous 10% ammonium chloride (10 ml) and filtered through Celite; the residue was washed with ethyl acetate. The combined filtrate was dried (Na_2SO_4) and evaporated *in vacuo* to yield a syrup (2.65 g), which crystallised from benzene–light petroleum (904 mg, 27%). Recrystallisation from benzene–light petroleum yielded the pure diol (30) (718 mg, 22%), m.p. 85—85.5°, identical (m.p., $[\alpha]_D$, i.r.) with the diol prepared by reduction of the ethyne (3).

From a similar reaction of the sugar (2) (1.0 g) and ethylmagnesium bromide was isolated a mixture of diols (30) and (28) (1.05 g, 94%), which was acetylated with acetic anhydride (3 ml) and pyridine (5 ml). The crude mixture of diacetates (31) and (29) (1.32 g, 98%) was analysed by n.m.r. spectroscopy (100 MHz; $CDCl_3$; signals at δ 2.05 and 2.14). The ratio of (31) to (29) was 63 : 37.

(b) *In tetrahydrofuran.* The reaction was repeated as above, with tetrahydrofuran in place of ether. The syrupy product (3.25 g, 97%) crystallised from benzene–light petroleum yielding the diol (30) (1.55 g, 46%), which was recrystallised from benzene–light petroleum to give needles (1.21 g, 36%), m.p. 85—85.5°. The mother liquors were evaporated to yield a syrup, a portion of which (110 mg) was acetylated as before. The syrupy product was purified by sublimation (90—110° and 0.10 mmHg); δ (100 MHz; $CDCl_3$) 0.90 (2t, superimposed, CH_2Me) and 2.04, 2.08, and 2.13 (3s, COMe). Integration of the singlets at δ 2.04 and 2.13 indicated a ratio of (29) to (31) of 46.5 : 53.5. If one assumes no fractionation during the short-path distillation of the acetates, the ratio of the diols (28) and (30) produced in the reaction is about 30 : 70.

We thank Drs. H. S. Isbell and E. Zissis for samples of reference compounds and the S.R.C. for a research studentship (to A. D. D.) and for n.m.r. spectra measured at the P.C.M.U., Harwell.

[5/1046 *Received*, 2nd *June*, 1975]