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Acetolysis of 2,4-*O*-benzylidene-D-*xylo*-hex-5-enitol derivatives *

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ABSTRACT

Acetolysis of (*Z*)-1-*O*-acetyl-2,4-*O*-benzylidene-5,6-dideoxy-6-*C*-(2,4-dichlorophenyl)-3-*O*-methanesulfonyl-D-*xylo*-hex-5-enitol afforded (*E*)-1,2,4-tri-*O*-acetyl-5,6-dideoxy-6-*C*-(2,4-dichlorophenyl)-3-*O*-methanesulfonyl-D-*xylo*- and -L-*arabino*-hex-5-enitol, 2-*C*-[(*R*)-acetoxy(2,4-dichlorophenyl)methyl]-3,6-di-*O*-acetyl-2-deoxy-4-*O*-methanesulfonyl-β-L-*galacto*-hexopyranosylbenzene and 6-*O*-acetyl-2-deoxy-2-*C*-[(*R*)-(2,4-dichlorophenyl)hydroxymethyl]-4-*O*-methanesulfonyl-β-L-*galacto*-hexopyranosylbenzene 3,7-(cyclic sulfate). The scope of this rearrangement was studied further on compounds with a 4-methoxybenzylidene instead of a benzylidene group, and a phenyl instead of a 2,4-dichlorophenyl group. In the latter reaction, in addition to 2-*C*-[(*R*)-acetoxy(phenyl)methyl]-3,4,5-tri-*O*-acetyl-2-deoxy-β-L-*galacto*-hexopyranosylbenzene, 1(*S*)-2-*C*-[(*R*)-acetoxy(phenyl)methyl]-1,3,4,5,6-penta-*O*-acetyl-2-deoxy-1-phenyl-L-gulitol was formed, the structure of which was established by X-ray analysis.

INTRODUCTION

We have described[1] the rearrangement of 2,4-*O*-benzylidene-D-*xylo*-hex-5-enitols into *C*-glycosylbenzene derivatives on acetolysis and suggested a mechanism for this new reaction. Further derivatives have now been synthesised and submitted to acetolysis in order to prove the validity of this mechanism and to investigate the scope and limitations of this rearrangement.

RESULTS AND DISCUSSION

In the mechanism suggested[1] for the rearrangement of 2,4-*O*-benzylidene-D-*xylo*-hex-5-enitol derivatives, an allylic ion was the key intermediate. Since an

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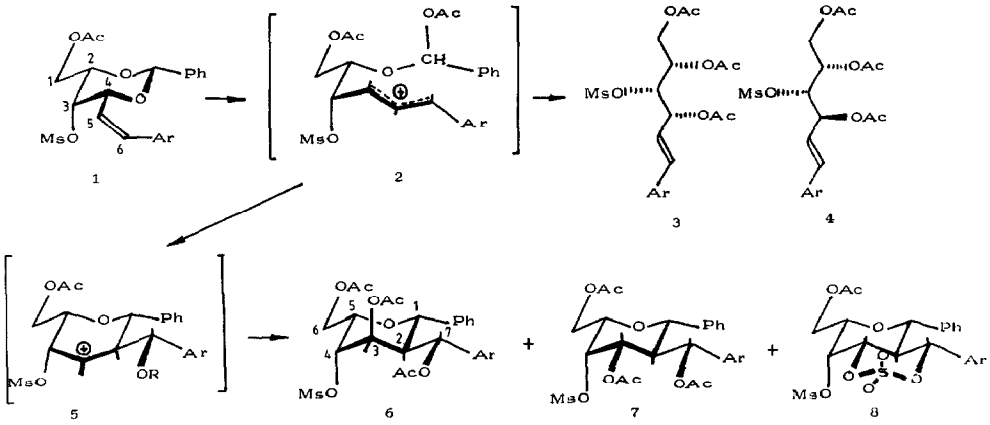


electron-withdrawing group in the α-position in this allylic system should strongly influence its reactivity *. Thus, acetolysis of the 1-*O*-acetyl-4-*O*-mesyl derivative[2] **1**, using sulfuric acid in acetic anhydride[1,3], gave (TLC) a complex mixture of products, from which the acyclic D-*xylo*- (**3**) and L-*arabino* (**4**) isomers and the branched-chain *C*-L-(*galacto*-hexopyranosyl)benzene derivative (**7**) and its 3,7-cyclic sulfate (**8**) were isolated in yields of 8.4, 4.4, 5.8, and 14.0%, respectively. Compounds **3** and **4** can result from the attach of acetic anhydride on C-4 of the allylic ion **2**, whereas **7** and **8**' can be formed via the rearranged cyclic carbonium ion **5**. The 14.0% yield of the cyclic sulfate **8** contrasts with that (2%) of the cyclic sulfate formed when there was a 4-*O*-methyl substituent[1]. The $J_{5,6}$ value of 15.9 Hz proves the *E* configuration of the double bond in **3** and **4**. There are only small differences between the chemical shifts of the ^1H and ^{13}C resonances and the *J* values of these compounds, which suggests that they are C-4 epimers. The D-*xylo* and L-*arabino* configurations for **3** and **4**, respectively, were assumed on the basis of their $[\alpha]_D$ values (+29° and −30°, respectively) in comparison with data for acyclic analogues[4]. Despite the fact that the cyclic L-*gulo* derivative **6** could not be isolated, NMR spectroscopy suggested that it might be present in several fractions, which could not be resolved by column chromatography.

In further experiments, we sought to establish that *C*-glycosyl derivatives which contained a substituted phenyl group as the aglycon can be obtained via this rearrangement. Therefore, 2,4-*O*-(4-methoxybenzylidene)-D-glucitol (**9**) was prepared by the reaction of D-glucitol with 4-methoxybenzaldehyde dimethyl acetal in *N*,*N*-dimethylformamide in the presence of *p*-toluenesulfonic acid. D-Glucitol preferentially forms 2,4-*O*-benzylidene acetals[5] and the NMR data of **9** as well as

* In the original paper[1], only the corresponding 1,4-ditosylate was investigated, but the tosyloxy group at C-1 triggered other reactions that interfered with the rearrangement process.

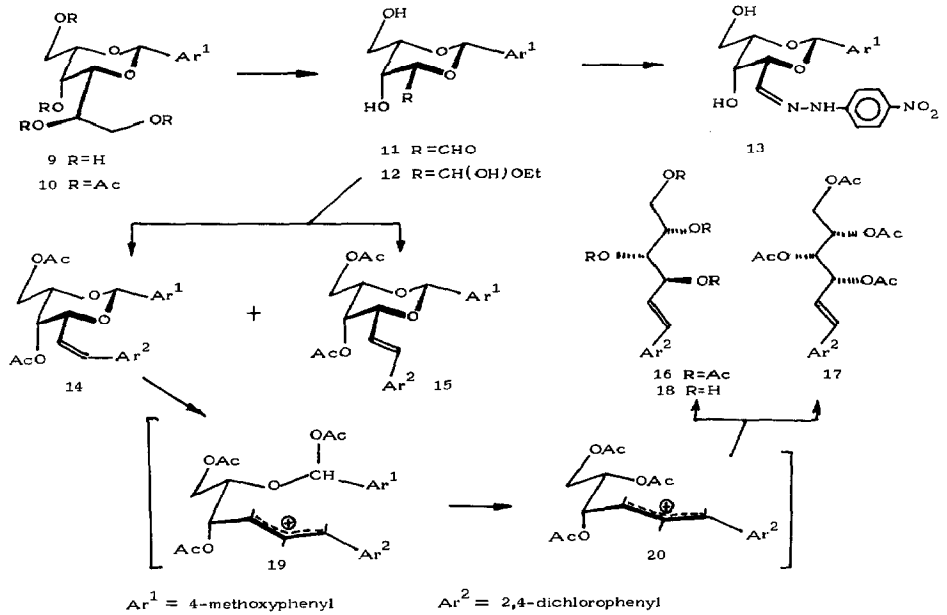
those of its tetra-acetate **10** were in agreement with the proposed structure. Oxidation of **9** with sodium periodate gave the L-xylose derivative **11**, which could be isolated as a mixture of its ethyl hemiacetals **12** and characterised as the 4-nitrophenylhydrazone **13**.

Crude **11** was coupled in tetrahydrofuran–*N*,*N*-dimethylformamide with the ylid prepared from 2,4-dichlorophenyltriphenylphosphonium chloride and potassium *tert*-butoxide to yield, after acetylation, the corresponding *Z* (**14**) and *E* (**15**) isomers in the ratio 15:1.

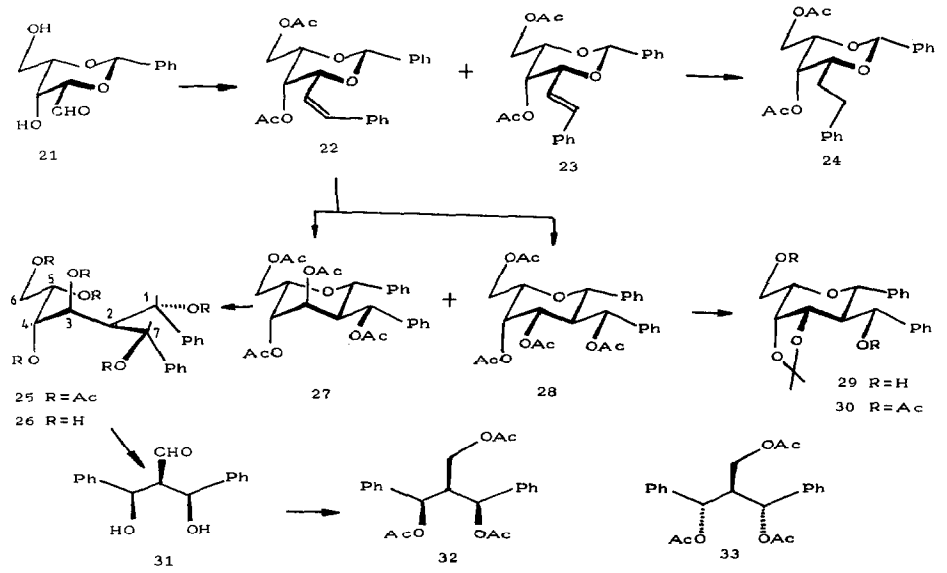
Acetolysis of **14**, as for **1**, gave (TLC) only two compounds, namely the acyclic tetra-acetates **16** and **17**. Since **17** was identical with the D-*xylo* isomer[1], and the NMR data indicated that the two isomers differed only in the chirality at C-4, **16** must possess the L-*arabino* configuration. In order to confirm these assignments of structures, **16** and **17** were each submitted to ozonolysis, followed by reduction with $NaBH_4$ and acetylation, to afford the expected penta-*O*-acetyl-L-arabinitol and -xylitol, respectively. The $[\alpha]_D$ values of **16** (−75°) and **17** (−35°) as well as that (−14°) of the deacetylated derivative **18** compared to that (+18°) of the corresponding D-*xylo* isomer[1] were in accord with the trend established[4] for acyclic L-*arabino* and D-*xylo* isomers. The fact that no rearrangement products (*C*-glycosyl derivatives) were formed might reflect the greater acid sensitivity of the 4-methoxyenzylidene group (Ar^1) compared to the benzylidene group and its rapid cleavage from the allyl intermediate **19**, yielding the two diastereomers **16** and **17** via **20**. Thus, the relative stability of the intermediate benzyl cation is crucial for the rearrangement reaction.

As a further model, the 5-*Z* isomer of the 6-*C*-phenyl derivative **22** was investigated, which was obtained together with the corresponding 5-*E* isomer **23** (*Z*,*E*-ratio 2:1) when 2,4-*O*-benzylidene-L-xylose[2] (**21**) was coupled with the ylid prepared from benzyltriphenylphosphonium chloride and potassium *tert*-butoxide. On hydrogenation over Pd/C, **22** and **23** each gave the phenethyl derivative **24** without reductive cleavage of the benzylidene group. This finding contrasts with that for the corresponding 6-*C*-(2,4-dichlorophenyl) analogue, from which the benzylidene group was split off under identical conditions[2]. This cleavage was probably catalysed by hydrochloric acid formed in traces from the 2,4-dichlorophenyl group during hydrogenation.

Acetolysis of **22** afforded (TLC) a complex mixture of products from which the rearranged *C*-glycosylphenyl derivative **28** and the branched-chain diphenyl derivative **25** could be isolated after 24 h in yields of 10 and 16.5%, respectively. The L-*galacto* configuration of **28** was evident from its ^1H NMR spectrum, which was almost identical with that[1] of the analogue having a 2,4-dichlorophenyl group at C-6. Further proof of the structure of **28** was obtained after deacetylation and treatment of the resulting tetraol with 2-methoxypropene in acetone in the presence of *p*-toluenesulfonic acid[6], when the 3,4-*O*-isopropylidene derivative **29** was formed. The NMR data of **29** as well those of its diacetate **30** were in full agreement[7] with the proposed structures.



The NMR spectra of the acyclic derivative **25** were in agreement with its proposed structure, but did not indicate the configurations of the newly formed chiral centres at C-1 and C-7. Therefore, **25** was deacetylated and the product (**26**)



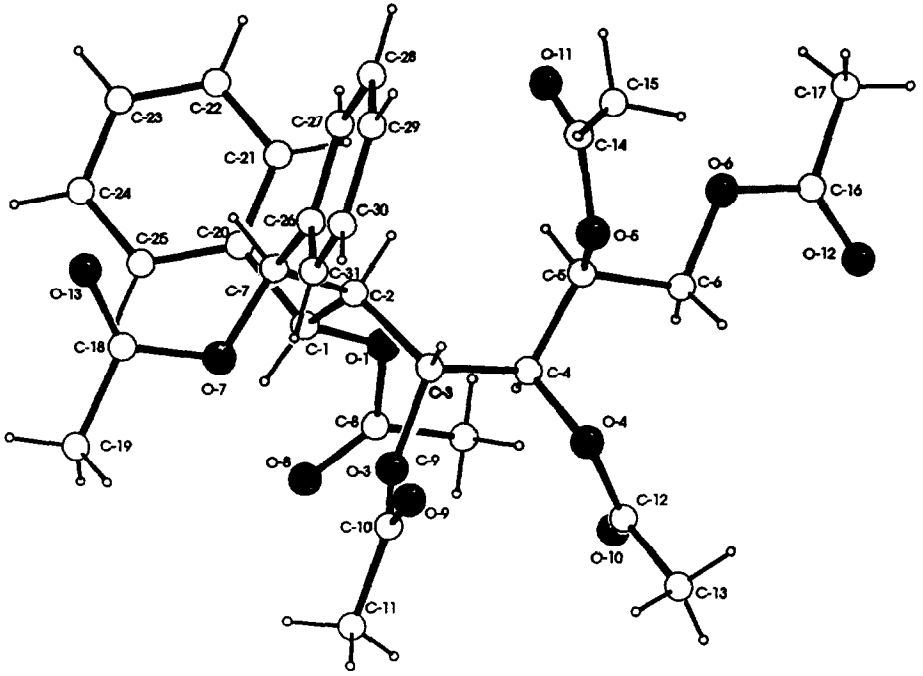


Fig. 1. PLUTO plot and numbering scheme for **25**.

was oxidised with sodium periodate to give an aldehyde (**31**) that was reduced without isolation, using borohydride, and then acetylated to give a symmetrical triacetate, which could be either **32** or **33**. Since **25** can be formed only by cleavege of the intermediate **27**, the configuration of C-1 and C-7 should correspond to **32**. Since cleavage of the ether in **27** could proceed with retention, or with inversion, of configuration at C-5, the structure of **25** was determined by crystallography which proved the configuration of all the chiral centres (see Fig. 1 and Tables I–III).

In solution and in the solid state, the carbon skeleton of **25** adopts essentially the same "sickle" conformation in which C-2 and C-5 as well as O-2 and O-4 are synclinal, whereas H-3 and H-4 are antiperiplanar ($J_{3,4}$ 9.1 Hz). Furthermore, AcO-3 and AcO-7 are in a 1,3-parallel arrangement which is tolerated in acetylated alditols[8]. The coupling constants, calculated[9] from the torsion angles determined in the X-ray study, are given together with the measured values in Table IV.

The fact that acetolysis of **22** gave neither the acyclic 5(*E*)-ene derivatives (the analogues of **16** and **17**), nor the *C*-(L-*gulo*-hexopyranosyl) derivative **27**, but only the product (**25**) of acetolysis, prompted an investigation of the course of this reaction. Thus, the products of the reaction after 0.5, 1, 2, 4, 8, 24, 48, and 78 h were analysed by GLC and the ratios are given in Table V; a representative chromatogram (4 h) is depicted in Fig. 2. The data obtained indicate that **22** is

TABLE I

Bond lengths (Å) with esds for **25**

O-1–C-1	1.455(3)	O-10–C-12	1.179(5)	C-12–C-13	1.495(6)
O-1–C-8	1.341(4)	O-11–C-14	1.197(4)	C-14–C-15	1.478(5)
O-3–C-3	1.452(3)	O-12–C-16	1.184(5)	C-16–C-17	1.462(6)
O-3–C-10	1.346(4)	O-13–C-18	1.170(5)	C-18–C-19	1.489(6)
O-4–C-4	1.452(3)	C-1–C-2	1.544(4)	C-20–C-21	1.372(5)
O-4–C-12	1.345(4)	C-1–C-20	1.523(4)	C-20–C-25	1.369(5)
O-5–C-5	1.439(3)	C-2–C-3	1.551(4)	C-21–C-22	1.406(6)
O-5–C-14	1.344(4)	C-2–C-7	1.535(4)	C-22–C-23	1.349(7)
O-6–C-6	1.426(4)	C-3–C-4	1.534(4)	C-23–C-24	1.387(7)
O-6–C-16	1.326(4)	C-4–C-5	1.520(4)	C-24–C-25	1.397(6)
O-7–C-7	1.448(3)	C-5–C-6	1.511(4)	C-26–C-27	1.377(5)
O-7–C-18	1.365(4)	C-7–C-26	1.515(4)	C-26–C-31	1.359(5)
O-8–C-8	1.202(4)	C-8–C-9	1.490(5)	C-27–C-28	1.409(5)
O-9–C-10	1.201(5)	C-10–C-11	1.480(6)	C-28–C-29	1.370(6)
				C-29–C-30	1.401(7)
				C-30–C-31	1.372(6)

TABLE II

Bond angles (°) with esds for **25**

C-1–O-1–C-8	117.6(4)	O-3–C-10–C-11	111.3(6)
C-3–O-3–C-10	118.9(4)	O-9–C-10–C-11	124.3(6)
C-4–O-4–C-12	116.4(4)	O-4–C-12–O-10	125.1(6)
C-5–O-5–C-14	117.8(4)	O-4–C-12–C-13	110.5(6)
C-6–O-6–C-16	115.8(4)	O-14–C-12–C-13	124.3(7)
C-7–O-7–C-18	116.2(4)	O-5–C-14–O-11	122.9(5)
O-1–C-1–C-2	106.4(3)	O-5–C-14–C-15	111.5(5)
O-1–C-1–C-20	108.3(4)	O-11–C-14–C-15	125.6(6)
C-2–C-1–C-20	112.5(4)	O-6–C-16–O-12	123.9(6)
C-1–C-2–C-3	113.8(4)	O-6–C-16–C-17	111.3(6)
C-1–C-2–C-7	109.2(4)	O-12–C-16–C-17	124.7(6)
C-3–C-2–C-7	112.8(4)	O-7–C-18–O-13	123.6(6)
O-3–C-3–C-2	109.2(3)	O-7–C-18–C-19	110.0(5)
O-3–C-3–C-4	104.9(4)	O-13–C-18–C-19	126.4(6)
C-2–C-3–C-4	116.1(4)	C-1–C-20–C-21	120.3(5)
O-4–C-4–C-3	105.2(4)	C-1–C-20–C-25	119.7(5)
O-4–C-4–C-5	109.2(4)	C-21–C-20–C-25	120.1(5)
C-3–C-4–C-5	115.8(4)	C-20–C-21–C-22	119.4(6)
O-5–C-5–C-4	108.7(4)	C-21–C-22–C-23	120.8(7)
O-5–C-5–C-6	109.3(4)	C-22–C-23–C-24	120.0(8)
C-4–C-5–C-6	110.9(4)	C-23–C-24–C-25	119.4(8)
O-6–C-6–C-5	106.9(4)	C-20–C-25–C-24	120.3(6)
O-7–C-7–c-2	107.1(4)	C-7–C-26–C-27	117.1(5)
O-7–C-7–C-26	112.0(4)	C-7–C-26–C-31	122.7(5)
C-2–C-7–C-26	115.3(4)	C-27–C-26–C-31	120.2(6)
O-1–C-8–O-8	123.4(5)	C-26–C-27–C-28	119.9(6)
O-1–C-8–C-9	110.0(5)	C-27–C-28–C-29	119.1(7)
O-8–C-8–C-9	126.6(6)	C-28–C-29–C-30	120.3(8)
O-3–C-10–O-9	124.3(6)	C-29–C-30–C-31	119.3(7)
		C-26–C-31–C-30	121.2(7)

TABLE III

Exocyclic torsion angles (°) with esds for **25**

O-4–C-4–C-3–O-3	−63.0(3)	C-11–C-10–O-3–C-3	−177.0(7)
O-5–C-5–C-4–O-4	−64.1(4)	C-12–O-4–C-4–C-3	123.3(5)
O-6–C-6–C-5–O-5	−66.7(4)	C-14–O-5–C-5–C-4	−139.1(5)
C-1–O-1–C-8–O-8	2.0(5)	C-14–O-5–C-5–C-6	99.8(5)
C-1–C-2–C-3–O-3	−43.2(4)	C-15–C-14–O-5–C-5	−167.7(6)
C-1–C-2–C-7–O-7	62.9(4)	C-16–O-6–C-6–C-5	177.6(5)
C-2–C-3–C-4–O-4	176.5(4)	C-17–C-16–O-6–C-6	179.3(7)
C-3–O-3–C-10–O-9	5.1(5)	C-18–O-7–C-7–C-2	−149.3(5)
C-3–C-2–C-1–O-1	−54.5(4)	C-19–C-18–O-7–C-7	176.4(6)
C-3–C-2–C-7–O-7	−64.6(4)	C-20–C-1–O-1–C-8	−100.0(4)
C-3–C-4–C-5–O-5	54.4(4)	C-20–C-1–C-2–C-3	−172.9(5)
C-4–O-4–C-12–O-10	2.6(5)	C-20–C-1–C-2–C-7	60.1(4)
C-4–C-3–C-2–C-1	75.1(4)	C-21–C-20–C-1–O-1	−57.6(5)
C-4–C-5–C-6–O-6	173.6(5)	C-21–C-20–C-1–C-2	59.6(5)
C-5–O-5–C-14–O-11	10.8(5)	C-22–C-21–C-20–C-1	−179.7(8)
C-5–C-4–C-3–O-3	176.3(5)	C-24–C-25–C-20–C-1	−179.6(8)
C-5–C-4–C-3–C-2	55.8(4)	C-25–C-20–C-1–O-1	122.4(6)
C-6–O-6–C-16–O-12	−2.2(5)	C-25–C-20–C-1–C-2	−120.4(6)
C-6–C-5–C-4–O-4	55.9(4)	C-26–C-7–O-7–C-18	83.5(5)
C-6–C-5–C-4–C-3	174.4(5)	C-26–C-7–C-2–C-1	−171.8(5)
C-7–O-7–C-18–O-13	−3.6(5)	C-26–C-7–C-2–C-3	60.7(4)
C-7–C-2–C-1–O-1	178.5(4)	C-27–C-26–C-7–O-7	−163.2(6)
C-7–C-2–C-3–O-3	81.9(4)	C-27–C-26–C-7–C-2	74.0(5)
C-7–C-2–C-3–C-4	−159.9(4)	C-28–C-27–C-26–C-7	177.8(7)
C-8–O-1–C-1–C-2	138.8(4)	C-30–C-31–C-26–C-7	−176.6(9)
C-9–C-8–O-1–C-1	−177.1(6)	C-31–C-26–C-7–O-7	15.0(5)
C-10–O-3–C-3–C-2	−125.7(5)	C-31–C-26–C-7–C-2	−107.7(6)
C-10–O-3–C-3–C-4	109.2(5)		

converted first into the two cyclic ethers **27** and **28**. After 30 min, < 2% of **22** remained and only one further product (peak A; 10%) was present. However, **27** is unstable and reacted further to yield the more-stable hexa-acetate **25** which, after 24 h, became the main product of the reaction.

TABLE IV

Measured and calculated vicinal coupling constants for **25**

	Measured	Calculated	Torsion angle (°)
$J_{1,2}$	10.0	11.5	−177.2
$J_{2,3}$	0.7	0.4	76.3
$J_{2,7}$	2.8	1.9	60.0
$J_{3,4}$	9.1	9.7	−176.5
$J_{4,5}$	2.1	1.5	52.3
$J_{5,6a}$	5.6	2.5	−65.8
$J_{5,6b}$	7.0	10.0	173.3

TABLE V

Relative intensities (%) of GLC peaks of the reaction mixture obtained on acetolysis (Ac_2O/H_2SO_4) of **22**

Reaction time (h)	Peaks [a]						
	27	**28**	**A**	**B**	**25**	**C**	**D**
	t_R^b 1.09	1.10	1.14	1.37	1.42	1.43	1.46
0.5	35	50	10	–	+ [c]	+	–
1	50	30	15	–	+	+	–
2	35	20	20	+	10	+	+
4	20	20	20	+ + [d]	15	10	10
8	+	20	20	5	30	15	10
24	–	20	15	5	40	15	5
48	–	15	5	5	50	15	5
72	–	10	+ +	+ +	70	15	+ +

[a] Compounds lettered as in Fig. 2. [b] Retention times relative to that of **22** (24.57 min). [c] Traces. [d] Less than 2%.

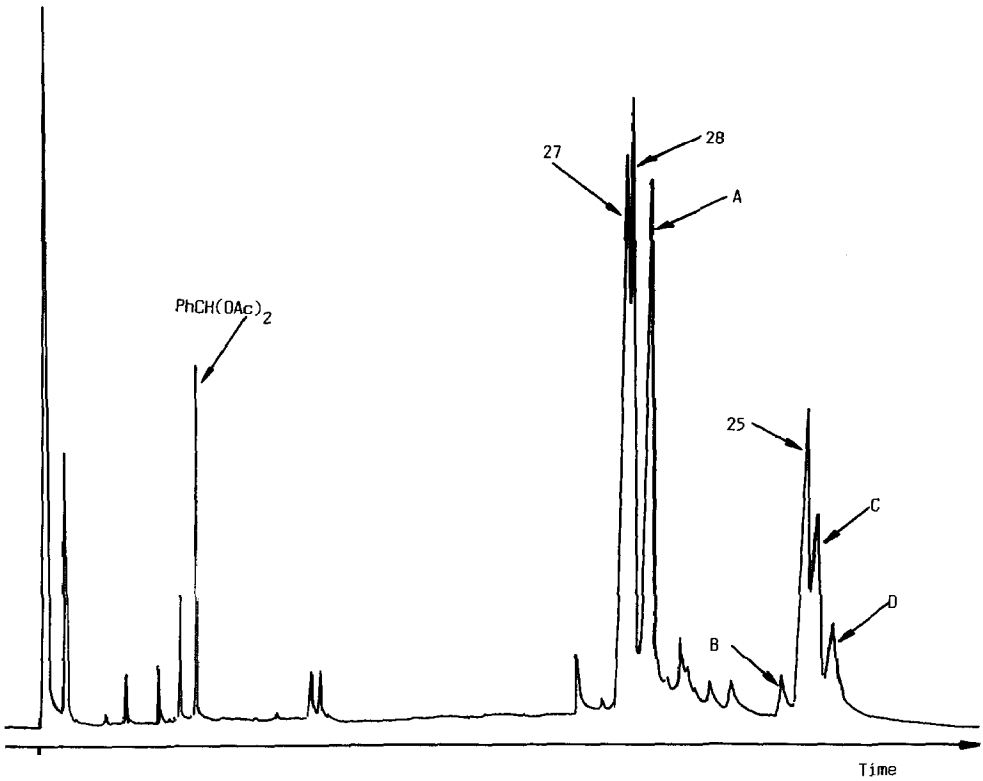


Fig. 2. GLC of the reaction mixture obtained on acetolysis (Ac_2O/H_2SO_4) of **22** after 4 h. Retention times (min): diacetoxy(phenyl)methane (8.34), **27** (27.00), **28** (27.11), **A** (27.95), **B** (33.75), **25** (34.86), **C** (35.28), and **D** (35.92).

EXPERIMENTAL

General methods.—Organic solutions were dried with Na_2SO_4 and concentrated under diminished pressure. Reactions were carried out at room temperature (20°C) and optical rotations were determined at 20°C on 1% solutions in $CHCl_3$ unless stated otherwise. TLC was performed on Kieselgel G with *A*, EtOAc; EtOAc–hexane mixtures (*B*, 1:1; *C*, 1:2); and *D*, 9:1 EtOAc–EtOH; with detection using 1:1 0.1 M $KMNO_4$–M H_2SO_4 at 200°C. For column chromatography, Kieselgel 60 was used. NMR spectra were recorded with a Bruker 250 spectrometer at 250 (^1H) and 62.9 MHz (^{13}C) on solutions in $CDCl_3$ (internal Me_4Si) unless stated otherwise. Signal multiplicities of the ^{13}C NMR spectra were obtained from DEPT experiments. Full assignment of the ^{13}C NMR spectrum of **25** was gained from a ^{13}C–^1H heteronuclear chemical shift correlation 2D measurement performed using the standard microprogram of the Bruker DISNMR software. H-3′,5′,6′ refer to the protons of the 2,4-dichlorophenyl group and double-primed numbers to the phenyl group. GLC was conducted with a Hewlett–Packard 5720A gas chromatograph, using an Ultra 1 capillary column coated with cross-linked methyl silicon gum (50 × 0.2 nm × 0.33 nm film thickness); temperature 3°C · min^{-1} from 200 to 260°C; carrier gas, N_2 at a flow rate of 20 mL · min^{-1}.

X-ray data collection, structure solution, and refinement.—Intensity data were collected from a transparent crystal of approximate size 0.35 × 0.50 × 0.50 mm on an Enraf–Nonius CAD-4 diffractometer, using graphite-monochromated CuK_α radiation, $\omega/2\theta$ scans ($1.5 < \theta < 75.0$). The intensities of three check reflections, recorded every 60 min, remained constant throughout data collection. A total of 3726 unique reflections was measured. The intensity data were corrected for Lorentz and polarisation effects. No absorption corrections were applied. The structure was solved by direct methods and refined by anisotropic full-matrix least-squares for the non-H atoms. The positional parameters for the H atoms were generated from assumed geometries. H Atomic parameters were included in structure factor calculations, but they were not refined. Their isotropic temperature factors were derived from those of the attached carbon atoms [B(H) = B(C) + 1, Å^2]. 388 parameters were refined in the final cycle, and the number of observations [$F^2 > 3\sigma(F^2)$] and the maximum shift/esd were 3291 and 0.12, respectively. The final *R* factors were $R_o = 0.045$, $R_w = 0.064$, $w = 1/[(\sigma F_o)^2 + (0.002\ F_o)^2]$ (σF from counting statistics); $R_{tot} = 0.054$ for all (3726) reflections. The highest peak and lowest minimum in the final difference map were 0.065 and −0.43 e/Å^3, respectively. Atomic scattering factors for neutral atoms and anomalous dispersion coefficients were taken from International Tables[10]. All calcula-

tions were performed on a PDP-11/34 minicomputer, using the E.N. SDP-plus program package[11] and local programs *.

Acetolysis of (Z)-*1*-O-*acetyl-2,4*-O-*benzylidene-5,6-dideoxy-6*-C-(*2,4-dichlorophenyl*)-*3*-O-*methanesulfonyl*-D-xylo-*hex-5-enitol* (**1**).—Sulfuric acid (2.5 mL) was added to a solution of **1**[2] (2.5 g) in acetic anhydride (2.5 mL) at 0°C. The solution was kept at room temperature for 20 h, then poured onto ice, and, after 20 min, extracted with $CHCl_3$, to give, after the usual processing, a syrup that was submitted to column chromatography (solvent *C*).

The fractions having R_f 0.40 gave, on concentration, 6-*O*-acetyl-2-deoxy-2-*C*-[(*R*)-(2,4-dichlorophenyl)hydroxymethyl]-4-*O*-methanesulfonyl-β-L-*galacto*-hexopyranosylbenzene 3,7-(cyclic sulfate) (**8**; 420 mg, 14%); $[\alpha]_D$ +43°; ν_{max}^{KBr} 3050 w, 2960 w, 1745 s, 1591 m, 1586 w, 1481 m, 1458 w, 1410 s, 1371 s, 1252 s, 1204 s, 1178 s, 1150 m, 1105 m, 1070 m, 986 m, 922 m, 905 m, 866 m, 833 m, 787 m, 764 m, 700 w, 655 w, 588 w, 567 w, 542 w, 490 w, and 465 w cm^{-1}. ^1H NMR data: δ 7.1–6.9 (m, 8 H, aromatic), 6.26 (d, 1 H, H-7), 5.35–5.25 (m, 2 H, H-3,4), 4.39 (d, 1 H, H-1), 4.30 (dd, 1 H, H-6a), 4.21 (dd, 1 H, H-6b), 4.11 (dd, 1 H, H-5), 3.27 (s, 3 H, MsO), 3.17 (ddd, 1 H, H-2), and 2.06 (3, 3 H, AcO); $J_{1,2}$ 9.8, $J_{2,3}$ 10.5, $J_{2,7}$ 11.1, $J_{5,6a}$ 7.0, $J_{5,6b}$ 5.9, $J_{6a,6b}$ 11.3 Hz. Anal. Calcd for $C_{22}H_{22}Cl_2O_{10}S_2$: C, 45.44; H, 3.81; Cl, 12.19; S, 11.02. Found: C, 45.56; H, 3.95; Cl, 12.00; S, 10.86.

Eluted next was (*E*)-1,2,4-tri-*O*-acetyl-5,6-dideoxy-6-*C*-(2,4-dichlorophenyl)-3-*O*-methanesulfonyl-D-*xylo*-hex-5-enitol (**3**; 210 mg, 8.4%); $[\alpha]_D$ +29°, R_f 0.35. NMR data: ^1H, δ 7.44 (d, 1 H, H-6′), 7.31 (d, 1 H, H-3′), 7.16 (dd, 1 H, H-5′), 7.01 (d, 1 H, H-6), 6.14 (dd, 1 H, H-5), 5.52 (dd, 1 H, H-4), 5.28 (q, 1 H, H-2), 5.06 (t, 1 H, H-3), 4.26 (dd, 1 H, H-1a), 4.10 (dd, 1 H, H-1b), 3.01 (s, 3 H, MsO), 2.04, 2.02, and 2.01 (3 s, each 3 H, 3 AcO); $J_{1a,1b}$ 11.9, $J_{1a,2} = J_{1b,2} = J_{2,3} = J_{3,4} = 5.3$, $J_{4,5}$ 8.3, $J_{5,6}$ 15.9, $J_{3',5'}$ 2.0, $J_{5',6'}$ 8.5 Hz; ^{13}C, δ 170.3, 169.7, 169.2 (3 s, 3 CH_3COO), 134.8, 133.9, 132.1 (3 s, C-1′,2′,4′), 132.0, 129.5, 127.9, 127,4, 124,6 (5 d, C-5,6,3′,5′,6′), 78.5, 71.5, 68.1 (3 d, C-2,3,4), 61.6 (t, C-1), 38.9 (q, SCH_3), 20.8, 20.6, 20.5 (3 q, 3 $COCH_3$).

Eluted third was (*E*)-1,2,4-tri-*O*-acetyl-5,6-dideoxy-6-*C*-(2,4-dichlorophenyl)-3-*O*-methanesulfonyl-L-*arabino*-hex-5-enitol (**4**; 110 mg, 4.4%); $[\alpha]_D$ −30°, R_f 0.30. NMR data: ^1H, δ 7.38 (d, 1 H, H-6), 7.31 (d, 1 H, H-3), 7.15 (dd, 1 H, H-5′), 6.93 (d, 1 H, H-6), 6.02 (dd, 1 H, H-5), 5.64 (dd, 1 H, H-4), 5.26 (q, 1 H, H-2), 4.99 (dd, 1 H, H-3), 4.35 (dd, 1 H, H-1a), 3.98 (dd, 1 H, H-1b), 3.01 (s, 3 H, MsO), 2.11, 2.06, and 2.00 (3 s, each 3 H, 3 AcO); $J_{1a,1b}$ 11.9, $J_{1a,2} = J_{1b,2} = J_{2,3} = 5.0$, $J_{3,4}$ 6.1, $J_{4,5}$ 6.9, $J_{5,6}$ 15.9, $J_{3',5'}$ 2.0, $J_{5',6'}$ 8.5 Hz; ^{13}C, δ 170.3, 169.6, 169.5 (3 s, 3 CH_3COO), 134.8, 133.9, 132.0 (3 s, C-1′,2′,4′), 130.6, 129.6, 127.8, 127.4, 124.8 (5 d, C-5,6,3′,5′,6′),

* Lists of atomic co-ordinates, structured factors, and anisotropic thermal parameters for the non-H atoms have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, Netherlands. Reference should be made to No. BBA/DD/514/*Carbohydr. Res.*, 239 (1993) 117–132.

78.8, 71.8, 68.7 (3 d, C-2,3,4), 61.4 (t, C-1), 38.9 (q, SCH_3), 21.0, 20.7, and 20.6 (3 q, 3 $COCH_3$). Anal. Calcd for $C_{19}H_{22}Cl_2O_9S$: C, 45.88; H, 4.45; Cl, 14.25; S, 6.44. Found for **3**: C, 45.92; H, 4.55; Cl, 14.19; S, 6.38. Found for **4**: C, 46.03; H, 4.60; Cl, 14.18; S, 6.27.

Eluted last was 2-*C*-[(*R*)-acetoxy(2,4-dichlorophenyl)methyl]-3,6-di-*O*-acetyl-2-deoxy-4-*O*-methanesulfonyl-β-L-*galacto*-hexopyranosylbenzene (**7**; 175 mg, 5.8%); mp 194–196°C (from hexane); $[\alpha_D]$ −26°; R_f 0.2. ^1H NMR data: δ 7.39 (m, 5 H, Ph), 7.27 (d, 1 H, H-3′), 7.14 (dd, 1 H, H-5′), 7.01 (d, 1 H, H-6′), 5.61 (d, 1 H, H-7), 5.52 (dd, 1 H, H-3), 5.05 (d, 1 H, H-4), 4.47 (d, 1 H, H-1), 4.27 (dd, 1 H, H-6a), 4.14 (dd, 1 H, H-6b), 4.01 (dd, 1 H, H-5), 3.08 (s, 3 H, MsO), 3.07 (ddd, 1 H, H-2), 2.26, 2.06, and 1.56 (3 s, each 3 H, 3 AcO); $J_{1,2}$ 10.3, $J_{2,3}$ 11.3, $J_{2,7}$ 1.2, $J_{3,4}$ 3.2, $J_{5,6a}$ 6.2, $J_{5,6b}$ 7.3, $J_{6a,6b}$ 11.1, $J_{3',5'}$ 2.0, $J_{5',6'}$ 8.4 Hz. Anal. Calcd for $C_{26}H_{28}Cl_2O_{10}S$: C, 51.74; H, 4.67; Cl, 11.75; S, 5.31. Found: C, 51.71; H, 4.63; Cl, 11.69; S, 5.18.

2,4-O-(4-Methoxybenzylidene)-D-*glucitol* (**9**).—A solution of D-glucitol (9 g) in *N,N*-dimethylformamide (20 mL) and 4-methoxybenzaldehyde dimethyl acetal (14 mL) was stirred in the presence of *p*-toluenesulfonic acid (0.1 g) for 20 h. The resulting precipitate was filtered off and washed with MeOH. The combined filtrate and washings were neutralised with Et_3N, then Kieselgel 60 (20 g) was added, and the solvent was evaporated from the slurry. Column chromatography (solvent *D*) of the residue and recrystallisation from EtOH gave **9** (5.3 g, 35%); mp 172–174°C; $[\alpha]_D$ +16° (Me_2SO); R_f 0.3. NMR data (Me_2SO-d_6): ^1H, δ 7.42, 6.90 (2 d, each 2 H, aromatic), 5.48 (s, 1 H, OCHO), 3.86 (s, 3 H, OMe), 3.85–3.30 (m, 8 H, H-1a–6b); ^{13}C δ 159.8 (s, C-4′), 131.6 (s, C-1′), 128.2 (d, C-3′), 113.5 (d, C-2′), 100.5 (d, OCHO), 81.2, 79.8 (2 d, C-2,4), 69.6, 62.1 (2 d, C-3,5), 63.2, 61.4 (2 t, C-1,6), 55.5 (q, OCH_3). Anal. Calcd for $C_{14}H_{20}O_7$: C, 55.99; H, 6.71. Found: C, 55.91; H, 6.76.

1,3,5,6-Tetra-O-*acetyl-2,4-O-(4-methoxybenzylidene)*-D-*glucitol* (**10**).—Acetylation of **9** (1 g) with acetic anhydride (3 mL) in pyridine (5 mL) gave, after the usual processing, **10** (1.4 g, 89.7%); mp 118–120°C; $[\alpha]_D$ −11°; R_f 0.3 (solvent *C*). ^1H NMR data: δ 7.42, 6.90 (2 d, each 2 H, aromatic), 5.63 (s, 1 H, OCHO), 5.25–5.10 (m, 2 H, H-3,5), 4.6–4.0 (m, 6 H, H-1a,1b,2,4,6a,6b), 3.80 (s, 3 H, MeO), 2.10, 2.06, 2.05, and 2.03 (4 s, each 3 H, 4 AcO). Anal. Calcd for $C_{22}H_{28}O_{11}$: C, 56.40; H, 6.02. Found: C, 56.33; H, 6.06.

2,4-O-(4-Methoxybenzylidene)-L-*xylose* (**11**).—To a stirred slurry of **9** (5.35 g) and $NaHCO_3$ (0.2 g) in 1,4-dioxane (50 mL) was added a warm (40°C) solution of $NaIO_4$ (4.1 g) in water (12 mL). The mixture was stirred for 1 h at room temperature, and the inorganic salts were collected and washed with EtOH (20 mL). The combined filtrate and washings were concentrated to give crude **11** (4.09 g, 85%), which was purified by column chromatography (solvent *A*) to give, after treatment with EtOH–ether, **11** as a mixture of its ethyl hemiacetals (**12**; 2.85 g, 51%); mp 96–110°C; $[\alpha]_D$ −5°; R_f 0.30 (solvent *A*). ^1H NMR data: δ 7.44, 6.91 (2 d, each 2 H, aromatic), 5.47 (s, 1 H, OCHO), 4.65 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1), 3.8–3.3 (m, 7 H, H-2,3,4,5a,5b and OCH_2CH_3), 3.35 (s, 3 H, MeO), and 1.12 (t, 3

H, *J* 7.1 Hz, OCH_2CH_3). Anal. Calcd for $C_{15}H_{22}O_7$ C, 57.31; H, 7.05. Found: C, 57.17; H, 7.11.

A slurry of crude **11** (100 mg) and 4-nitrophenylhydrazine (100 mg) in MeOH (10 mL) was boiled for 30 min under reflux. The resulting solution was concentrated and the residue purified by column chromatography (solvent *A*) to give **13** (110 mg, 73.3%); mp 152–154°C (from ether); R_f 0.65. ^{1}H NMR data ($CDCl_3$ + Me_2SO-d_6): δ 10.5 (s, 1 H, NH), 8.07, 7.48, 7.04, 6.87 (4 d, each 2 H, aromatic), 7.49 (d, 1 H, H-1), 5.69 (s, 1 H, OCHO), 4.58 (dd, 1 H, H-2), 4.39 (s, 1 H, HO-5), 4.19 (d, 1 H, HO-3), 4.02 (m, 1 H, H-4), 3.88–3.78 (m, 3 H, H-3,5a,5b), and 3.80 (s, 3 H, MeO); $J_{1,2}$ 6.3, $J_{2,3}$ 1.5, $J_{3,OH}$ 7.7, $J_{5,OH}$ 6.0 Hz. Anal. Calcd for $C_{19}H_{21}N_3O_7$ C, 56.56; H, 5.24; N, 10.41. Found: C, 56.38; H, 5.32; N, 10.59.

(Z)- (**14**) *and* (E)-*1,3-Di-*O*-acetyl-5,6-dideoxy-6-*C*-(2,4-dichlorophenyl)-2,4-*O*-methoxybenzylidene-*D*-xylo-hex-5-enitol* (**15**).—To a stirred slurry of [(2,4-dichlorophenyl)methyl]triphenylphosphonium chloride (3.4 g) in dry tetrahydrofuran (35 mL) and *N*,*N*-dimethylformamide (7 mL) was added potassium *tert*-butoxide (0.85 g). The orange solution was stirred for 1 h at room temperature, crude **11** (1.7 g) was added, and, after 1 h, the mixture was diluted with water and extracted with EtOAc. The combined extracts were washed with brine and dried, and the solvent was evaporated. The residue was dissolved in pyridine (7 mL) and acetic anhydride (5 mL) was added. After 20 h, the mixture was processed in the usual way. Column chromatography (solvent *C*) then gave **14** (1.82 g, 58.1%); mp 82–84°C (from hexane); $[\alpha]_D$ +108°; R_f 0.60. NMR data: ^{1}H, δ 7.45–7.20 (m, 5 H, aromatic), 6.89 (d, 2 H, aromatic), 6.71 (d, 1 H, H-6), 5.80 (dd, 1 H, H-5), 5.58 (s, 1 H, OCHO), 5.02 (s, 1 H, H-3), 4.60 (d, 1 H, H-4), 4.30–4.05 (m, 3 H, H-1a,1b,2), 3.79 (s, 3 H, MeO), 2.21 and 2.04 (2 s, each 3 H, AcO); $J_{4,5}$ 8.3, $J_{5,6}$ 11.6 Hz; ^{13}C, δ 170.4 (CH_3COO), 160.1 (C-4′), 134.2, 134.2, 133.1, 130.9, 130.6, 129.6, 129.3, 127.6, 127.4, 126.8 (C-5,6 and aromatic), 113.5 (C-2′,6′), 100.4 (OCO), 75.5, 74.7, 65.8 (C-2,3,4), 62.3 (C-1), 55.2 (OCH_3), 20.6 and 20.5 ($OCOCH_3$).

Eluted second was **15** (0.12 g, 3.8%); mp 98–100°C (from hexane); $[\alpha]_D$ 0°; R_f 0.50. ^{1}H NMR data: δ 7.55–7.15 (m, 5 H, aromatic), 7.06 (d, 1 H, H-6), 6.93 (d, 2 H, aromatic), 6.07 (dd, 1 H, H-5), 5.73 (s, 1 H, OCHO), 5.13 (t, 1 H, H-3), 4.75 (dd, 1 H, H-4), 4.45–4.10 (m, 3 H, H-1a,1b,2), 3.82 (s, 3 H, MeO), 2.09, and 2.08 (2 s, each 3 H, 2 AcO); $J_{2,3} = J_{3,4} = 1.4$, $J_{4,5}$ 4.8, $J_{5,6}$ 15.9 Hz. Anal. Calcd for $C_{24}H_{24}Cl_2O_7$: C, 58.19; H, 4.88; Cl, 14.31. Found for **14**: C, 58.27; H, 5.02; Cl, 14.16. Found for **15**: C, 58.35; H, 5.06; Cl, 14.22.

Acetolysis of **14**.—Sulfuric acid (1.3 mL) was added to a stirred solution of **14** (1.3 g) in acetic anhydride (13 mL) at 0°C. The solution was processed as described for **1**, to give a syrup, TLC (solvent *C*) of which revealed only two components with R_f 0.60 and 0.55, which were isolated by column chromatography.

Eluted first was (*E*)-tetra-*O*-acetyl-5,6-dideoxy-6-*C*-(2,4-dichlorophenyl)-*L*-*arabino*-hex-5-enitol (**16**; 230 mg, 19.0%); $[\alpha]_D$ −75°. ^{1}H NMR data: δ 7.45–7.15 (m, 3 H, aromatic), 7.01 (d, 1 H, H-6), 6.02 (dd, 1 H, H-5), 5.55–5.35 (m, 3 H, H-2,3,4), 4.27 (dd, 1 H, H-1a), 4.02 (dd, 1 H, H-1b), 2.10, 2.07, 2.06, and 2.05 (4 s,

each 3 H, 4 AcO); $J_{1a,b}$ 11.6, $J_{1a,2}$ 5.2, $J_{1b,2}$ 6.9, $J_{4,5}$ 8.3, $J_{5,6}$ 15.8 Hz. Anal. Calcd for $C_{20}H_{22}Cl_2O_8$: C, 52.07; H, 4.80; Cl, 15.37. Found: C, 51.88; H, 4.93; Cl, 15.18.

Eluted second was (*E*)-tetra-*O*-acetyl-5,6-dideoxy-6-*C*-(2,4-dichlorophenyl)-D-*xylo*-hex-5-enitol (**17**; 110 mg, 9%), identical with the product described earlier[1].

Structural elucidation of **16** *and* **17**.—A stream of O_3/O_2 was passed into a cooled (−70°C) solution of **16** (200 mg) in CH_2Cl_2 (20 mL) until the colour turned blue (10 min). The solution was purged with N_2 to remove the excess O_3 and then concentrated. The residue was dissolved in MeOH (20 mL), and $NaBH_4$ (0.1 g) was added at 0°C. After stirring at 0 °C for 1.5 h, more $NaBH_4$ (0.05 g) was added, and stirring was continued at room temperature. After 2 h, the pH was adjusted to 2 with methanolic 2 M HCl, then the mixture was concentrated. Methanol (3 × 10 mL) was evaporated from the residue which was then treated with acetic anhydride (1 mL) in pyridine (2 mL). After 20 h at room temperature, the solvent was evaporated and the residue purified by column chromatography (solvent *C*) to yield penta-*O*-acetyl-L-arabinitol (114 mg, 73%); $[\alpha]_D$ −37°; lit.[12] $[\alpha]_D$ −38° (MeOH).

Similar treatment of **17** (100 mg) yielded penta-*O*-acetylxylitol (61 mg, 76%). The NMR data of both compounds were identical with those published[13].

(E)-*5,6-Dideoxy-6-C-(2,4-dichlorophenyl)*-L-arabino-*hex-5-enitol* (**18**).—Methanolic M NaOMe (0.01 mL) was added to a solution of **17** (200 mg) in MeOH (5 mL). After 24 h at room temperature, Na ions were removed with Varion KS (H^+) resin to give, after filtration, evaporation of the solvent, and treatment of the residue with ether, **18** (103 mg, 81%); mp 128–130°C; $[\alpha]_D$ −14° (MeOH); R_f 0.60 (solvent *D*). Anal. Calcd for $C_{12}H_{14}Cl_2O_4$: C, 49.16; H, 4.81; Cl, 24.19. Found: C, 49.09; H, 4.92; Cl, 24.08.

(Z)- (**22**) *and* (E)-*1,3-Di*-O-*acetyl-2,4*-O-*benzylidene-5,6-dideoxy-6*-C-*phenyl*-D-xylo-*hex-5-enitol* (**23**).—To a stirred slurry of benzyltriphenylphosphonium chloride (4 g) in dry tetrahydrofuran (40 mL) and *N,N*-dimethylformamide (10 mL) was added potassium *tert*-butoxide (1.2 g). The orange solution was stirred for 1 h at room temperature, then crude 2,4-*O*-benzylidene-L-xylose[2] (**21**; 2.4 g) was added. The mixture was processed as described for **14** and **15**, to give, after column chromatography (solvent *C*), **22** (1.53 g, 38.6%); mp 67–69°C (from ether–hexane); $[\alpha]_D$ −21°; R_f 0.55. ^1H NMR data: δ 7.70–7.15 (m, 10 H, aromatic), 6.72 (d, 1 H, H-6), 5.62 (dd, 1 H, H-5), 5.60 (s, 1 H, OCHO), 5.03 (s, 1 H, H-3), 4.77 (d, 1 H, H-4), 4.30-4.00 (m, 3 H, H-1a,1b,2), 2.15 and 2.02 (2 s, each 3 H, 2 AcO); $J_{4,5}$ 8.0, $J_{5,6}$ 11.5 Hz.

Eluted second was **23** (0.73 g, 18.2%); mp 102–104°C (from ether–hexane); $[\alpha]_D$ −21°; R_f 0.55. ^1H NMR data: δ 7.75–7.10 (m, 10 H, aromatic), 6.75 (d, 1 H, H-6), 6.06 (dd, 1 H, H-5), 5.74 (s, 1 H, OCHO), 5.10 (s, 1 H, H-3), 4.68 (d, 1 H, H-4), 4.45–4.10 (m, 3 H, H-1a,1b,2), 2.08 and 2.04 (2 s, each 3 H, 2 AcO); $J_{4,5}$ 5.0, $J_{5,6}$ 16.0 Hz. Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found for **22**: C, 69.65; H, 6.13. Found for **23**: C, 69.62; H, 6.15.

Acetolysis of **22**.—A solution of **22** (940 mg) in acetic anhydride (10 mL) and

sulfuric acid (1 mL) was treated as described for **1**. After 14 h, the following products were isolated by column chromatography (solvent *C*) from the complex mixture. Evaporation of the fractions having R_f 0.45 gave 2-*C*-[(*R*)-acetoxy(phenyl)methyl]-3,4,5-tri-*O*-acetyl-2-deoxy-β-L-*galacto*-hexopyranosylbenzene (**28**; 120 mg, 10.2%); $[\alpha]_D$ −19°. NMR data: ^{1}H, δ 7.70–7.05 (m, 8 H, aromatic), 6.83 (d, 2 H, aromatic), 5.65 (d, 1 H, H-7), 5.43 (dd, 1 H, H-3), 5.34 (dd, 1 H, H-4), 4.44 (d, 1 H, H-1), 4.20–3.90 (m, 3 H, H-5,6a,6b), 2.79 (ddd, 1 H, H-2), 2.15, 2.13, 2.00, and 1.56 (4 s, each 3 H, 4 AcO); $J_{1,2}$ 10.6, $J_{2,3}$ 11.3, $J_{2,7}$ 1.6, $J_{3,4}$ 3.5, $J_{4,5}$ 0.9 Hz; ^{13}C, δ 170.4, 170.2, 169.7, 169.4 (each s, COO), 139.5, 138.7 (each s, C-1′,1″), 128.9, 128.8, 127.9, 127.0, 124.4 (5 d, C-2′,3′,4′,2″,3″,4″), 80.0, 73.9, 69.0, 66.5 (4 d, C-1,3,4,5,7), 62.0 (t, C-6), 46.9 (d, C-2), 20.7, 20.6, 20.5, and 20.4 (4 q, 4 OCO*C*H$_3$). Anal. Calcd for $C_{27}H_{30}O_9$; C, 65.04: H, 6.06 Found: C, 65.00; H, 6.11.

Evaporation of the fractions having R_f 0.40 gave (*1S*)-2-*C*-[(*R*)-acetoxy(phenyl)methyl]-1,3,4,5,6-penta-*O*-acetyl-2-deoxy-1-*C*-phenyl-L-gulitol (**25**; 235 mg, 16.5%); mp 176–177°C (from ether–hexane); $[\alpha]_D$ −16°. NMR data (acetone-d_6): ^{1}H, δ 7.50–7.05 (m, 10 H, aromatic), 6.02 (d, 1 H, H-1), 5.77 (dd, 1 H, H-4), 5.65 (dd, 1 H, H-3), 5.44 (ddd, 1 H, H-5), 5.35 (d, 1 H, H-7), 4.11 (dd, 1 H, H-6a), 3.72 (dd, 1 H, H-6b), 2.71 (ddd, 1 H, H-2), 2.17, 2.13, 2.09, 2.02, 1.96, and 1.59 (6 s, each 3 H, 6 AcO); $J_{1,2}$ 10.0, $J_{2,3}$ 0.7, $J_{2,7}$ 2.8, $J_{3,4}$ 9.1, $J_{4,5}$ 2.1, $J_{5,6a}$ 5.6, $J_{5,6b}$ 7.0, $J_{6a,b}$ 11.4 Hz; ^{13}C, δ 170.6, 170.5, 170.4, 169.8, 169.5, 169.3 (6 s, 6 CH_3COO), 139.7, 139.6 (2 s, C-1′,1″), 129.7, 129.6, 129.5, 128.7, 128.6, 126.8 (6 d, C-2′,3′,4′,2″,3″,4″), 74.9, 74.6, 73.1, 69.0, 68.6 (5 d, C-1,3,4,5,7), 62.3 (t, C-6), 49.0 (d, C-2), 21.2, 21.0, 20.8, 20.7, 20.6, and 20.5 (6 q, 6 OCO*C*H$_3$).

Crystal data: fw = 600.6; a = 9.957(1), b = 16.500(1), c = 19.603(2) Å (from the setting angles of 25 reflections [29 < θ < 32°]), V = 3220.8(9) Å^3, orthorhombic space group: $P2_12_12_1$ (No. 19), Z = 4, F_{000} = 1272, D (calcd) = 1.238 g cm^{-3}, μ (CuK_α, λ = 1.54184 Å) = 7.63 cm^{-1}, T = 23°C. Anal. Calcd for $C_{31}H_{36}O_{12}$: C, 61.98; H, 6.04. Found: C, 61.95; H, 6.05.

GLC investigation of the acetolysis reaction of **22**.—Sulfuric acid (0.1 mL) was added to a solution of **22** (100 mg) in acetic acid (1 mL) at 0°C, then the temperature was raised to 20°C, and samples (0.1 mL) were taken from the reaction mixture at 0.5, 1, 2, 4, 8, 24, 48, and 72 h, diluted with water (1 mL), and extracted with $CHCl_3$ (10 mL). The organic solution was washed with aq 5% $NaHCO_3$ (5 mL), dried, and subjected to GLC. The results are depicted in Fig. 2 and summarised in Table IV.

*1,3-Di-*O*-acetyl-2,4-*O*-benzylidene-5,6-dideoxy-6-*C*-phenyl-*D*-xylo-hexitol* (**24**).—A solution of **22**, **23**, or a mixture thereof (0.3 g) in EtOH (20 mL) was hydrogenated in the presence of 10% Pd/C (0.05 g) for 2 h. In TLC (solvent *C*), the spot of **22** changed only its colour. The solution was filtered, concentrated, and treated with hexane to give **24** (0.3 g, 100%); mp 146–147°C; $[\alpha]_D$ +23°. ^{1}H NMR data: δ 7.7–7.2 (m, 10 H, aromatic), 5.68 (s, 1 H, OCHO), 5.04 (t, 1 H, H-3), 4.4–3.9 (m, 4 H, H-1a,1b,2,4), 2.85 (m, 2 H, H-6a,b), 2.21, 2.11 (2 s, each 3 H, 2 AcO), 2.1–1.7

(m, 2 H, H-5a,b); $J_{2,3} = J_{3,4} = 1.5$ Hz. Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.32; H, 6.57. Found: C, 69.19; H, 6.41.

1(S)-2-Deoxy-2-C-[(R)-hydroxy(phenyl)methyl]-1-phenyl-L-gulitol (**26**).—Methanolic M NaOMe (0.05 mL) was added to a solution of **25** (350 mg) in MeOH (10 mL). After 2 h at room temperature, Na ions were removed with Varion KS (H^+) resin to give, after concentration of the filtrate, **26** (159 mg, 78%); mp 152–154°C (from ether–hexane); $[\alpha]_D$ −17° (MeOH); R_f 0.6 (solvent *D*). NMR data (Me_2SO-d_6): ^1H, δ 7.45–7.10 (m, 10 H, aromatic), 4.83 (d, 1 H, H-1), 4.45 (d, 1 H, H-7), 3.90 (dd, 1 H, H-3), 3.45 (ddd, 1 H, H-5), 3.37 (dd, 1 H, H-4), 3.24 (dd, 1 H, H-6a), 3.12 (dd, 1 H, H-6b), 2.18 (ddd, 1 H, H-2); $J_{1,2}$ 7.8, $J_{2,3}$ 2.3, $J_{2,7}$ 4.0, $J_{3,4}$ 3.7, $J_{4,5}$ 4.0, $J_{5,6a}$ 4.6, $J_{5,6b}$ 7.0, $J_{6a,b}$ 10.9 Hz; ^{13}C, δ 145.2, 144.9 (2 s, C-1′,1″), 128.2, 128.1, 127.1, 127.0, 126,7, 125.9 (6 d, C-2′,3′,4′,2″,3″,4″), 73.4 (d, C-5), 72.9, 72.8 (2 d, C-4,7), 71.7 (d, C-1), 70.3 (d, C-3), 63.1 (t, C-6), and 54.2 (d, C-2). Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.44; H, 7.03.

2-Deoxy-2-C-[(R)-hydroxy(phenyl)methyl]-3,4-O-isopropylidene-β-L-galacto-hexopyranosylbenzene (**29**).—Methanolic M NaOMe (0.01 mL) was added to a solution of **28** (270 mg) in $CHCl_3$ (5 mL) and MeOH (1 mL). After 2 days at room temperature, the solution was neutralised with solid CO_2 and concentrated. The residue was dissolved in acetone (10 mL), and 2-methoxypropene (0.4 mL) and *p*-toluenesulfonic acid (20 mg) were added. After 20 h at room temperature, more 2-methoxypropene (0.2 mL) was added, followed, after 2 days, by Et_3N (0.5 mL). The mixture was concentrated and the residue purified by column chromatography (solvent *B*), to give **29** (135 mg, 67.3%); $[\alpha]_D$ −51°. NMR data: ^1H, δ 7.45–7.00 (m, 10 H, aromatic), 4.68 (dd, 1 H, H-3), 4.48 (bs, 1 H, H-7), 4.37 (d, 1 H, H-1), 4.1–3.65 (m, 4 H, H-4,5,6a,6b), 2.32 (m, 1 H, H-2), 1.19 and 1.17 (2 s, each 3 H, CMe_2); $J_{1,2}$ 9.7, $J_{2,3}$ 8.0, $J_{3,4}$ 5.5 Hz; ^{13}C, δ 143.5, 140.3 (2 s, C-1′,1″), 128.5, 128.2, 127.8, 127.5, 126.8, 125.4 (6 d, C-2′,3′,4′,2″,3″,4″), 108.8 (d, OCO), 80.5, 76.8, 72.8, 72.0, 71.8 (5 d, C-1,3,4,5,7), 63.2 (t, C-6), 51.6 (d, C-2), 27.8 and 26.5 (2 q, $C(CH_3)_2$). Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.32; H, 7.07. Found: C, 71.18; H, 6.92.

2-C-[(R)-Acetoxy(phenyl)methyl]-6-O-acetyl-2-deoxy-3,4-O-isopropylidene-β-L-galacto-hexopyranosylbenzene (**30**).—Acetylation of **29** (70 mg) with acetic anhydride (0.5 mL) in pyridine (1 mL) gave, after the usual processing and column chromatography (solvent *B*), **30** (60 mg, 69.8%) as a syrup; $[\alpha]_D$ −51°. NMR data: ^1H, δ 7.45–7.00 (m, 10 H, aromatic), 5.61 (d, 1 H, H-7), 4.53 (dd, 1 H, H-3), 4.37 (dd, 1 H, H-6a), 4.25 (dd, 1 H, H-6b), 4.20 (d, 1 H, H-1), 4.11 (dd, 1 H, H-4), 3.94 (ddd, 1 H, H-5), 2.53 (ddd, 1 H, H-2), 2.08, 2.03 (2 s, each 3 H, 2 AcO), 1.26 and 1.23 (2 s, each 3 H, CMe_2); $J_{1,2}$ 9.7, $J_{2,3}$ 7.9, $J_{2,7}$ 3.0, $J_{3,4}$ 5.5, $J_{4,5}$ 2.2, $J_{5,6a}$ 4.4, $J_{5,6b}$ 7.3, $J_{6a,b}$ 11.8 Hz; ^{13}C, δ 171.1, 169.6 (2 s, 2 CH_3COO), 140.0, 139.0 (2 s, C-1′,1″), 128.7, 128.5, 128.1, 127.6, 127.4, 125.9 (6 d, C-2′,3′,4′,2″,3″,4″), 109.3 (d, OCO), 80.0, 74.4, 74.0, 72.7, 72.2 (5 d, C-1,3,4,5,7), 64.5 (t, C-6), 50.1 (d, C-5), 27.8, 26.5 (2 q, $C(CH_3)_2$), 21.1 and 21.0 (2 q, 2 $OCOCH_3$). Anal. Calcd for $C_{26}H_{30}O_7$: C, 68.70; H, 6.65. Found: C, 68.58; H, 6.62.

1,3-Diacetoxy-2-acetoxymethyl-1,3-diphenyl-xylo-propane (**32**).—A solution of

$NaIO_4$ (0.3 g) in water (3 mL) was added to a stirred solution of **26** (150 mg) in 1,4-dioxane (10 mL). After 1 h, the precipitate was filtered off and $NaBH_4$ (0.1 g) was added to the filtrate followed, after 2 h, by more $NaBH_4$ (0.1 g). The pH of the solution was adjusted after 20 h to 2 with 2 M aq HCl, and the solution was then concentrated. Methanol (3 × 10 mL) was evaporated from the residue which was then treated with acetic anhydride (1 mL) in pyridine (2 mL). After 20 h at room temperature, the solvent was evaporated and the residue purified by column chromatography (solvent *C*), to give **32** (130 mg, 79.5%) as a syrup; $[\alpha]_D$ 0°; R_f 0.50. ^1H NMR data: δ 7.4–7.2 (m, 10 H, aromatic), 5.84 (d, 2 H, H-1,3), 4.30 (d, 2 H, H-4a,4b), 2.70 (d, 1 H, H-2), 2.05 (s, 6 H, AcO-1,3), 1.93 (s, 3 H, AcO); $J_{1,2} = J_{2,3} = J_{2,4} = 6$ Hz. Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.73; H, 6.29. Found: C, 68.60; H, 6.22.

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