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Rearrangement of unsaturated 2,4-*O*-benzylidenehexitol derivatives into *C*-glycosylbenzene derivatives *

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ABSTRACT

Acetolysis of (*Z*)-1,3-di-*O*-acetyl-2,4-*O*-benzylidene-6-*C*-(2,4-dichlorophenyl)-D-*xylo*-hex-5-enitol (**3**) afforded (*E*)-1,2,3,4-tetra-*O*-acetyl-6-*C*-(2,4-dichlorophenyl)-D-*xylo*-hex-5-enitol and 2-*C*-[(*R*)-acetoxy(2,4-dichlorophenyl)methyl]-3,4,6-tri-*O*-acetyl-2-deoxy-β-L-*galacto*- and -β-L-*gulo*-hexopyranosylbenzene. The mechanism of this new rearrangement was studied by exchanging the substituents at C-1 and C-3 in **3** and those of the aromatic ring attached to C-6.

INTRODUCTION

We have described [1] the synthesis of 6-*C*-(2,4-dichlorophenyl)-5,6-dideoxy-D-*xylo*-hexitol (**1**), a useful intermediate for the synthesis of potential inhibitors of HMG-CoA-reductase. In order to determine the influence of an unsaturated side chain on the biological activity, the corresponding (*Z*)-hex-5-enitol derivative **2** has been synthesized.

RESULTS AND DISCUSSION

It was expected that **2** would be obtained by acetolysis of the known [1] (*Z*)-2,4-*O*-benzylidenehex-5-enitol derivative **3** followed by deacetylation. However, acetolysis of **3** with sulfuric acid–acetic anhydride [2] gave a mixture of products from which the two branched-chain *C*-glycosylbenzene derivatives ("phenyl *C*-glycosides") **4** and **6**, in addition to the (*E*)-hex-5-enitol derivative **8**, were isolated in yields of 16, 14, and 22%, respectively.

The structures of **4**, **6**, and **8** were established by NMR and mass spectrometry. The EI-mass spectrum of **6** contained a cluster of weak peaks at *m/z* 566/568/570

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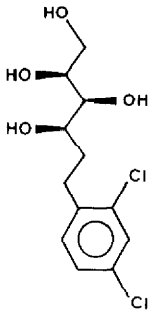

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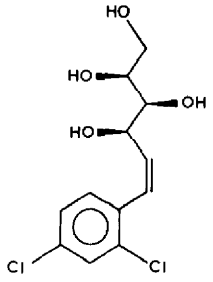

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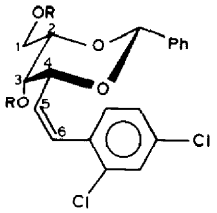
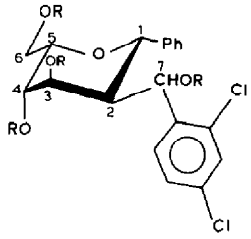


3 R = Ac

17 R = Ts



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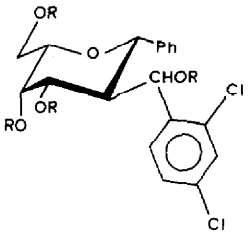
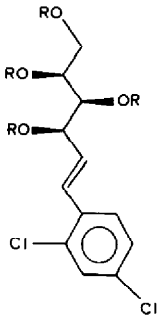
5 R = H



6 R = Ac

7 R = H



8 R = Ac

9 R = H

for molecular ions, which reflected the two chlorine substituents, and similar clusters at m/z 506/508/510, 446/448/450, and 386/388/390, corresponding to the loss of 1, 2, and 3 molecules of AcOH, respectively. From the exact mass of the ion with m/z 386 (386.05144, calcd for $C_{21}H_{16}ClO_3$: 386.04767), an elemental composition of $C_{27}H_{28}Cl_2O_9$ was deduced for **6**. The signals at δ 5.63 (s, PhC*H*) and 5.81 and 6.73 (2 d, J 11.6 Hz, (*Z*) HC=CH) of **3** were absent from the ^{1}H-NMR spectra of **4**, **6**, and **8**. The ^{1}H-NMR spectrum of **6** contained signals at δ 4.45 (d) and 5.59 (d) corresponding to H-1 and H-7 (for numbering see formulae). Unambigous assignment of these signals was made by semi-selective INEPT experiments [3]. Thus, selective excitation of the signals at δ 4.45 and 5.59 resulted in the appearance of signals for the *ipso* and the *ortho* carbons of the phenyl and dichlorophenyl rings, respectively, due to long-range ^{13}C,^{1}H couplings. The data $J_{1,2}$ 10.6 and $J_{2,3}$ 11.3 Hz proved the *trans*-diaxial arrangement of H-1,2,3 and the L-*galacto* configuration of **6**, which can be regarded as a branched-chain *C*-glycosylarene derivative. The NMR data ($J_{1,2}$ 10.3, $J_{2,3}$ 2.5 Hz) indicated **4** to have

TABLE I

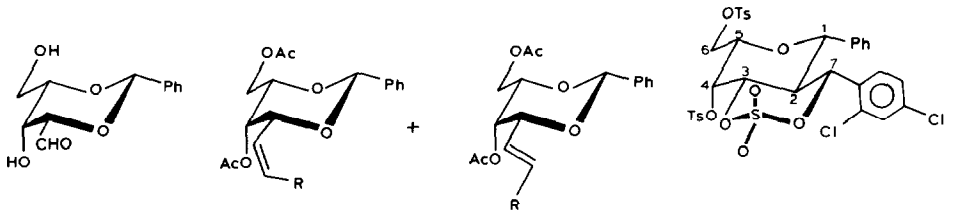
NOE data (%) for **4** and **6**

NOE at	Irradiated at **4**						**6**
	H-1	H-2	H-3	H-4	H-7	H-6′	H-1
H-1					4.6		
H-2			9.9		7.0	1.3	
H-3		13.4		9.6		1.1	4.7
H-4			11.7				−1.5
H-5	12.6			10.0			11.0
H-7	6.3	12.4	0.4			3.7	5.3
H-3′			0.4				
H-5′						11.3	
H-6′		4.6	2.3		4.2		
H-2″, 6″	7.3	6.0			0.8		7.0

H-1,2*ax*,*ax* and H-2,3*ax*,*eq*, i.e., the L-*gulo* configuration. The NOE data, shown in Table I for **4** and **6**, supported the above assignments. The configuration of the new chiral centre at C-7 could not be established unambiguosly from these data, but was determined by chemical modification (see below). The *E* configuration of the double bond in the tetra-acetate **8** was evident from the $J_{5,6}$ value of 15.7 Hz. The configuration at C-2,3,4 in **8** was also proved by the fact that deacetylation of **8** gave **9**, catalytic hydrogenation of which afforded **1**, whose structure has been established [1]. Deacetylation of **4** and **6** afforded the corresponding tetraols **5** and **7**, the NMR data of which were in full agreement with the proposed structures.

Thus, acetolysis of **3** causes a unique rearrangement, with the participation of the benzylidene group, resulting in the formation of a new C–C bond between the benzylidene carbon and the C-5 bridge of the double bond. Simultaneously, acetoxy groups are introduced at C-4 and C-6. These results differ significantly from those reported [4] for the partial acidic hydrolysis of 3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-phenylmethylene-α-D-*ribo*-hexofuranose and its analogs containing different substituents on the *exo*-methylene group. In this reaction, *C*-glycosyl compounds were formed by attack of O-6 on C-3 without the participation of the isopropylidene group. As this reaction depended strongly on the nature of the aromatic substituent (R) attached to the double bond, this parameter was investigated for the rearrangement mentioned above. Thus, **11–13** were synthesised and submitted to acetolysis.

2,4-*O*-Benzylidene-L-xylose [1] (**10**) was converted by a Wittig reaction into the corresponding 6-(pyrid-3-yl) (**11**), 6-(4-nitrophenyl) (**12** + **15**), and 6-(2-nitrophenyl) (**13** + **16**) hex-5-enitol derivatives. Whereas only the *Z*-isomer **11** was formed (isolated yield, 46%; no *E*-isomer **14** could be detected in the crude product by NMR spectroscopy), **12**(*Z*) and **15**(*E*) were formed in the ratio 3:1, and **13**(*Z*) and **16**(*E*) in the ratio ~2:1.



10 11 R = pyrid-3-yl 12 R = 4-nitrophenyl 13 R = 2-nitrophenyl 14 R = pyrid-3-yl 15 R = 4-nitrophenyl 16 R = 2-nitrophenyl 18

The (*Z*)-hex-5-enitol derivatives **11–13** were each submitted to acetolysis as for **3**, but no rearranged products could be detected (NMR spectroscopy). Thus, strongly electron-withdrawing groups in the aryl ring prevent rearrangement.

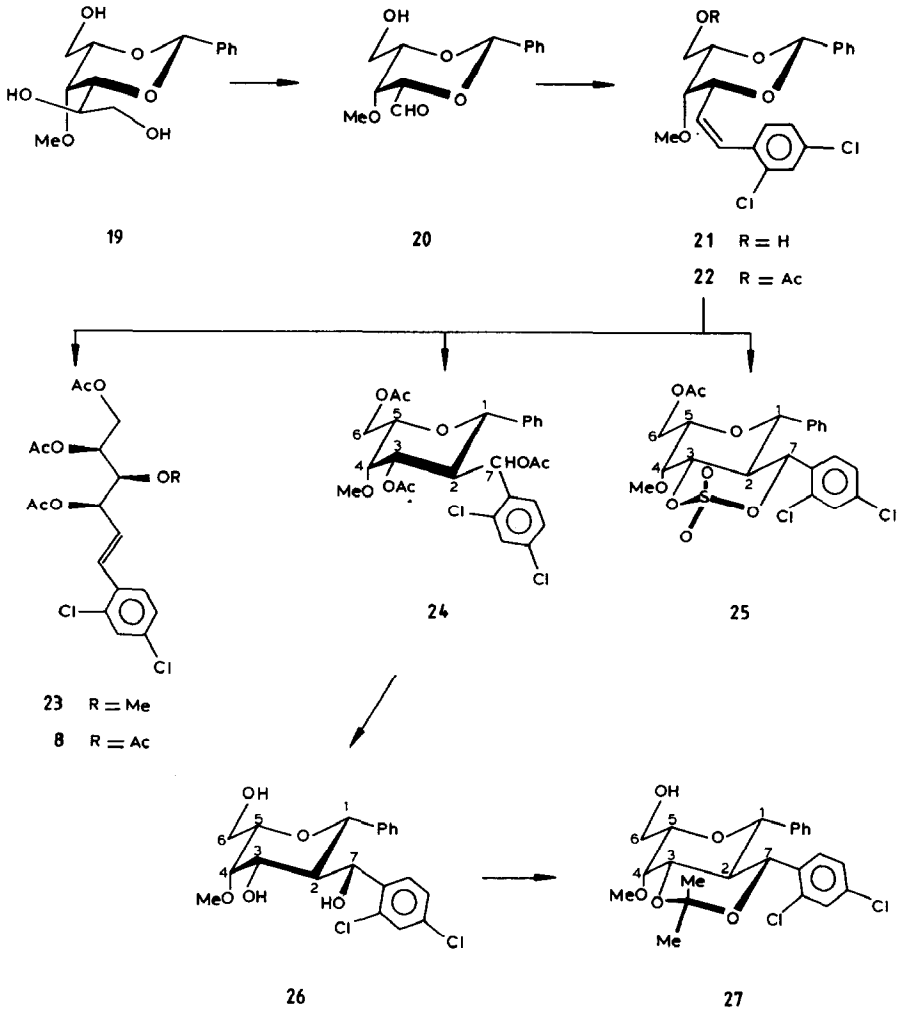
The influence of the 1,3-substituents of the carbohydrate skeleton was investigated next. Acetolysis of the known [1] 1,3-ditosylate **17** gave a more complex mixture of products than the 1,3-diacetate **3**, but the rearranged product **18** was isolated, which also contained a *trans*-fused 3,7-(cyclic sulfate). The presence of this cyclic sulfate was proved by the molecular-ion cluster at *m/z* 768/770/772 in the FAB-mass spectrum of **18** and the occurrence of SO_2 as a thermal degradation product in the EI-mass spectrum. The rigid *trans*-decalin-type system was indicated by the ^{1}H-NMR data ($J_{2,3}$ 10.9, $J_{2,7}$ 10.9, and $J_{1,2}$ 10.2 Hz) and NOE data (Table II). These data indicated the chirality of C-7 to be *R*. Despite the fact that only 2.7% of **18** was isolated, its formation is important in relation to the reaction mechanism (see below).

An analogue (**22**) of **3** was investigated, in which HO-3 was blocked by methylation and HO-1 by acetylation, and which was synthesised as follows. 2,4-*O*-Benzylidene-3-*O*-methyl-D-glucitol [5] (**19**) was oxidised with sodium periodate to give the aldehyde **20** (84.5%), characterised as the 4-nitrophenylhydrazone. Wittig reaction of **20** with the ylid prepared in situ from (2,4-dichlorophenylmethyl)triphenylphosphonium chloride afforded the (*Z*)-hex-5-en-

TABLE II

NOE data (%) for **18**

NOE at	Irradiated at			
	H-3	H-4	H-7	H-6′
H-1	4.4		3.6	
H-2				7.4
H-3		6.6	5.3	
H-4	6.7			
H-5	5.9	5.8		
H-6a		2.5		
H-7	9.4	−0.7		
H-5′				14.3

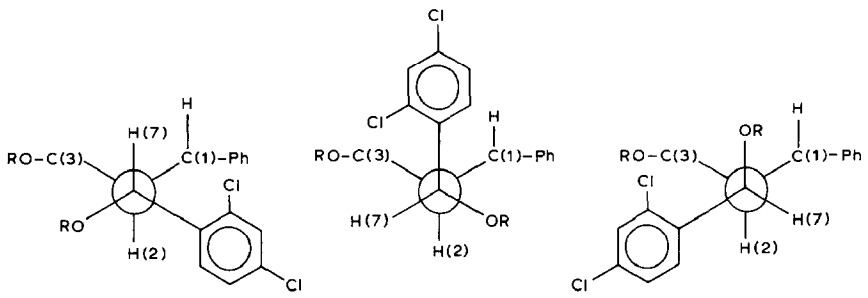


itol derivative **21** (42%). The corresponding 5*E* isomer could not be detected (NMR data). Acetylation of **21** then gave **22**. Acetolysis of **22** gave a complex mixture of products, and three components were isolated by column chromatography. The main component was a 2:1 mixture of the (*E*)-hex-5-enitol tri- (**23**) and tetra-acetate (**8**). The latter component was formed by loss of MeO-3 from **22** with retention of configuration during the acetolysis. The two other components isolated were the *C*-glycosylbenzene derivatives **24** (the analogue of **6**) and the bicyclic derivative **25** (the analogue of **18**). Thus, the rearrangement seems to be general for 2,4-*O*-benzylidene-D-*xylo*-hex-5-ene derivatives, having a 2,4-dichlorophenyl substituent attached to C-6 and a poor leaving group at C-1.

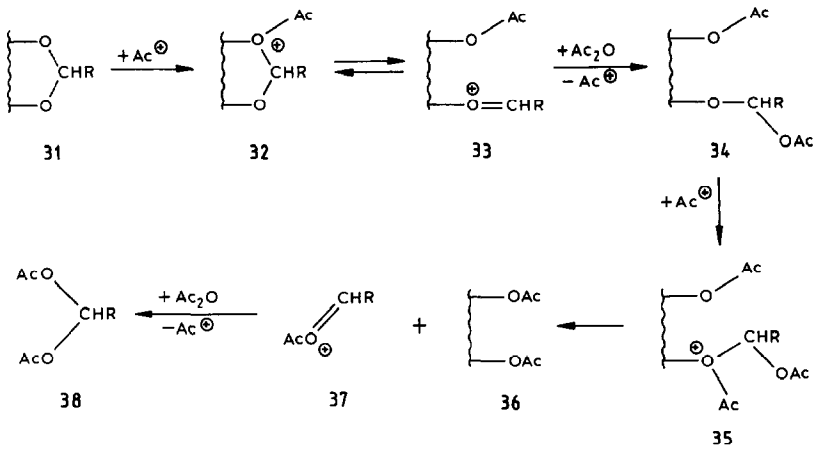
When the triol **26**, obtained by Zemplén deacetylation of **24**, was treated with 2-methoxypropene in the presence of *p*-toluenesulfonic acid, the 3,7-*O*-isopro-

pylidene derivative **27** was formed. The $^3J_{H,H}$ values and NOE data proved the presence of a *trans*-fused dioxolane ring in **27**. Irradiation of the axial Me of the isopropylidene group enhanced the intensity of the reasonances of H-3,7, and irradiation of H-7 enhanced the resonances of H-1,3 and the axial Me of the CMe_2 group. The decalin-type ring system in **27** is similar to that in **18** and **25**; consequently, C-7 has the *R* configuration, as, therefore, have the precursors **26** and **24**. The coupling constants for H-7 in **6**, **7**, and **24** are similar, so that the configuration of this centre is probably the same.

Knowing the configuration of C-7, the conformation around the C-2–C-7 bond can be based on the NMR data. The appropriate three Newman projections are depicted in **28–30**. Conformation **28** preponderates in the bicyclic compounds **18**, **25**, and **27**, since the $J_{2,7}$ values of 10.9, 11.2, and 10.8 Hz, respectively, indicate H-2,7 to be antiperiplanar. In the monocyclic compounds **6**, **7**, **24**, and **26**, the $J_{2,7}$ values are 1.7, 2.3, 1.1, and 2.7 Hz, respectively, consistent with a dihedral angle of 60° for H-2,7, as in the conformations **29** and **30**, of which the latter is less crowded and therefore more likely to be preponderant. This view was supported by the NOE data. Thus, irradiation of H-1 in **6** enhanced the intensity of the resonance of H-7. These protons are *gauche* in **30** but antiperiplanar in **29**. In **4**, the steric interaction of the axial AcO-3 and the dichlorophenyl group in the conformation **30** results in an equilibrium with equal proportions of conformations **28** and **30**, as reflected in the $J_{2,7}$ value of 6.8 Hz. When the acetyl groups of **4** are removed (→ **5**), the conformational equilibrium is shifted towards conformer **30**, as shown by the $J_{2,7}$ value of 2.5 Hz.

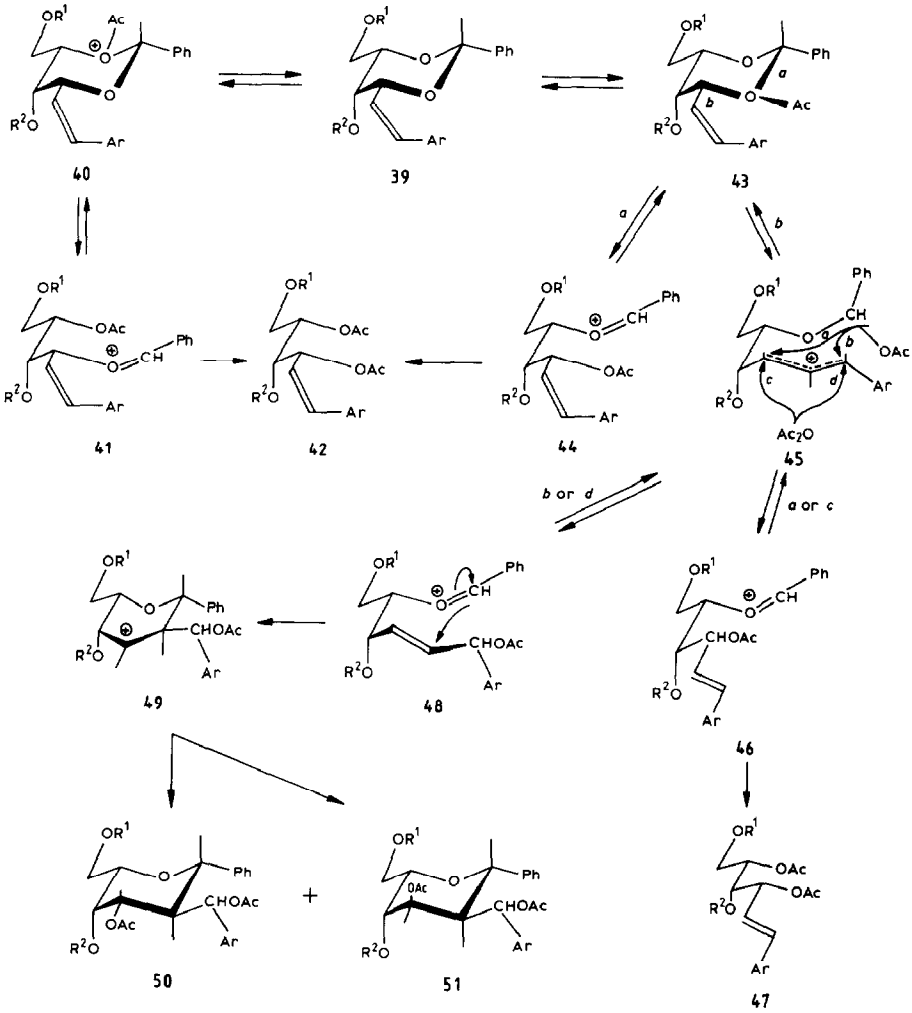


Mechanistic considerations.—The acetolysis of an acetal (**31**) starts with the attack of an acetylium ion on one of the acetal oxygen atoms (→ **32**). Cleavage of the acetal ring then yields an oxocarbonium ion (**33**), the stability of which depends on the nature of R. Acetylation of **33** affords the intermediate **34**, which has been isolated in several reactions [6–10]. Attack of a further acetylium ion (**34**) affords **35**, which yields the diacetate **36** and the acetoxycarbonium ion **37** that is converted into the geminal diacetate **38** of the original aldehyde, thereby regenerating the acetylium ion. If the acetal oxygen atoms in **31** are different chemically, then two intermediates **32**, but only one diacetate **36**, will be formed.



If the above mechanism is applied to the *O*-benzylidene derivative **39**, attack of the acetylium ion will yield **40** and **43**, each of which can yield the 5*Z* isomer of the acetylated tetraol **42** via the oxocarbonium ions **41** and **44**, respectively. However, in **43**, not only bond *a* but also bond *b* of the cyclic ion can be cleaved. Cleavage of bond *b* yields the allylic cation **45**, which should be stabilised by the attached aromatic substituent. In **45**, the acetoxy group located at the benzylic position can migrate to either end of the allylic system (route *a* or *b* in **45**). During this process, $Z \rightarrow E$ isomerisation [11] of the original double bond can take place, and the oxocarbonium ions **46** and **48** can be formed. However, these cations can be formed also by a two-step process, involving an intermolecular attack of acetic anhydride on the allylic system (routes *c* and *d* in **45**) and subsequent elimination of acetic anhydride. The configuration of the new chiral centre will depend on the pathway followed from **45**. Thus, route *a* gives the 4*R* isomer **46** and route *b* gives the 6*S* isomer **48**. On the other hand, if attack of the acetic anhydride occurred from the *exo*-side only, the 4*S* and the 6*R* isomers would be formed via routes *c* and *d*, respectively. Since acetolysis of **39** gave **47**, having the 4*R* configuration, **46** must have been formed via pathway *a* from **45**. Nevertheless, the 5*Z* isomer **42** could also be isomerised into the 5*E* isomer **47** under the strongly acidic conditions. However, separate experiments showed this process to be much slower.

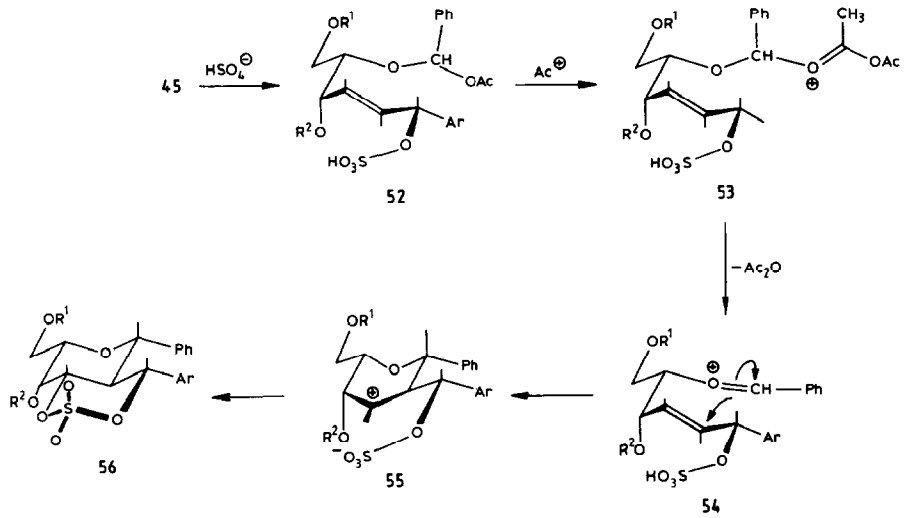
In **48**, the chiral centre at C-6 has the *R* configuration (see C-7 in **27**); thus, instead of migration of the acetoxy group (route *b* in **45**), the *exo*-attack of the acetic anhydride (route *d*) has taken place. Consequently, the cations **46** and **48** are formed by different mechanisms. In **48**, the benzylic cation can attack the double bond to yield the cyclic cation **49**. The ionic centre in **49** is flanked by relatively bulky, *trans* groups so that acetic anhydride can approach the cation from either side, and the isomers **50** and **51** are formed in almost equal proportions. Since C-6 of the allylic cation **45** is more susceptible to nucleophilic attack from the less-hindered "*exo*" side, it is not surprising that attack of the hydrosul-



fate anion afforded the sulfate **52**. The corresponding benzyl cation **54** can then be formed via an attack of an acetylium ion on **52** (→ **53**) and subsequent elimination of acetic anhydride. Cyclisation of **54** affords the carbonium ion **55**, which can be attacked intramolecularly by the sulfate ion from either side, but, since the *trans*-decalin system is the more stable, **56** is formed exclusively (see **18** and **25**).

EXPERIMENTAL

General methods.—Organic solutions were dried with Na_2SO_4 and concentrated under diminished pressure. Reactions were carried out at room temperature (20°) and optical rotations were determined at 20° 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; *D*, 1:3; *E*, 1:6); and EtOAc–MeOH (*F*, 9:1; *G*, 1:1); with detection using 1:1 0.1 M $KMnO_4$–M H_2SO_4 at 200°.

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. Selective INEPT spectra were measured with delays optimised for 7-Hz couplings (Δ_1 46 ms, Δ_2 56 ms). NOE measurements were made in the difference mode by the standard Bruker microprogram, using a low-power "line-by-line" saturation of multiplets. The ^1H-, ^{13}C-, ^1H–^{13}C-COSY, and NOE difference NMR spectra of **27** were obtained with a Varian VX-400 MHz instrument. H–3′,5′,6′ refer to the protons of the 2,4-dichlorophenyl group, and double-primed numbers to the phenyl groups.

Mass spectra were recorded with a Finnigan MAT 8430 mass spectrometer/SS300 data system: EI mode; electron energy, 70 eV; trap current, 0.5 mA; resolution, 1250/10%; high-resolution mass spectrometry at $R = 10000$ by the peak-matching technique, with perfluorokerosene as the reference standard; FAB mode, an Ion Tech FAB gun (8 kV), and a glycerol–*m*-nitrobenzyl alcohol (4:1) matrix were used.

5,6-Dideoxy-6-C-(2,4-dichlorophenyl)-D-xylo-*hexitol* (**1**).—Methanolic M sodium methoxide (0.05 mL) was added to a solution of **8** (90 mg) in MeOH (5 mL). After 24 h at room temperature, when TLC showed a single spot [R_F 0.4 (solvent *F*)], the solution was neutralised with solid CO_2, and hydrogenated in the presence of Pd–C (10%, 30 mg). After 3 h, the solution was filtered and concentrated, and the residue was recrystallised from EtOAc–ether to give **1** (49 mg, 82%), mp 112–114°, identical with that described [1].

(*Z*)-*5,6-Dideoxy-6-C-(2,4-dichlorophenyl)*-D-xylo-*hex-5-enitol* (**2**).—A solution of (*Z*)-2,4-*O*-benzylidene-5,6-dideoxy-6-*C*-(2,4-dichlorophenyl)-D-*xylo*-hex-5-enitol [1]

(1.9 g) in methanolic 0.2 M HCl (40 mL) was boiled under reflux for 10 min, then cooled, neutralised with solid $NaHCO_3$, filtered, and concentrated. Column chromatography (solvent *A*) of the residue gave **2** (1.2 g, 82%), mp 98–100° (from ether–hexane), R_F 0.4 (solvent *F*), $[\alpha]_D$ +22° (MeOH). ^{1}H-NMR data: δ 7.73 (d, 1 H, H-6′, 7.62 (d, 1 H, H-3′), 7.40 (dd, 1 H, H-5′), 6.53 (d, 1 H, H-6), 5.90 (dd, 1 H, H-5), 4.86, 4.42, and 4.28 (3 d, 3 H, HO-2,3,4), 4.50 (t, 1 H, HO-1), 4.26 (m, 1 H, H-4), and 3.5–3.25 (m, 4H, H-1a,1b,2,3); $J_{5,6}$ 11.7, $J_{4,5}$ 9.9, $J_{3',5'}$ 2.1, $J_{5',6'}$ 8.3 Hz.

Anal. Calcd for $C_{12}H_{14}Cl_2O_4$: C, 49.16; H, 4.81; Cl, 24.19. Found: C, 49.12; H, 4.86; Cl, 23.98.

Acetolysis of (Z)-*1,3-di-*O*-acetyl-2,4-*O*-benzylidene-5,6-dideoxy-6-C-(2,4-dichlorophenyl)-*D-xylo*-hex-5-enitol* [1] (**3**).—Sulfuric acid (0.5 mL) was added to a stirred solution of **3** (0.5 g) in acetic anhydride (5 mL) at 0°. The solution was kept at room temperature for 20 h, then poured onto ice (20 mL), and, after 20 min, extracted with $CHCl_3$, to give, after the usual processing, a syrup (0.5 g), TLC (solvent *C*) of which revealed components with R_F 0.5, 0.4, 0.3, and 0.2, which were isolated by column chromatography (solvent *D*).

The fraction (120 mg) with R_F 0.5 contained (NMR data) diacetoxyphenylmethane and several other components. The mixture decomposed on storage at room temperature to yield benzaldehyde and acetic acid.

Concentration of the fraction with R_F 0.4 gave (*E*)-tetra-*O*-acetyl-5,6-dideoxy-6-*C*-(2,4-dichlorophenyl)-D-*xylo*-hex-5-enitol (**8**; 110 mg, 22%), $[\alpha]_D$ −35°. ^{1}H-NMR data: δ 7.40 (d, 1 H, H-6′), 7.37 (d, 1 H, H-3′), 7.21 (dd, 1 H, H-5′), 6.95 (dd, 1 H, H-6), 6.05 (dd, 1 H, H-5), 5.64 (td, 1 H, H-4), 5.39 (dd, 1 H, H-3), 5.31 (dt, 1 H, H-2), 4.34 (dd, 1 H, H-1a), 3.99 (dd, 1 H, H-1b), 2.13, 2.11, 2.10, and 2.05 (4 s, 12 H, 4 AcO); $J_{1a,1b}$ 11.9, $J_{1a,2}$ 4.9, $J_{1b,2}$ 6.2, $J_{2,3}$ 4.6, $J_{3,4}$ 6.3, $J_{4,5}$ 6.6, $J_{5,6}$ 15.7, $J_{4,6}$ 1.1, $J_{3',5'}$ 2.1, $J_{5',6'}$ 8.2 Hz.

Anal. Calcd for $C_{20}H_{22}Cl_2O_8$: C, 52.07: H, 4.80: Cl, 15.37. Found: C, 51.96; H, 4.99; Cl, 15.21.

Concentration of the fractions with R_F 0.3 and treatment of the residue with ether–hexane gave 2-*C*-[(*R*)-acetoxy(2,4-dichlorophenyl)methyl]-3,4,6-tri-*O*-acetyl-2-deoxy-β-L-*galacto*-hexopyranosylbenzene (**6**; 83 mg, 14%), mp 184–186°. NMR data: ^{1}H δ 7.40 (m, 5 H, Ph), 7.26 (d, 1 H, H-3′), 7.11 (dd, 1 H, H-5′), 6.99 (d, 1 H, H-6′), 5.59 (d, 1 H, H-7), 5.55 (dd, 1 H, H-3), 5.33 (d, 1 H, H-4), 4.45 (d, 1 H, H-1), 4.15–4.05 (m, 1 H, H-5,6a), 3.98 (m, 1 H, H-6b), 2.97 (td, 1 H, H-2), 2.26, 2.14, 2.02, and 1.43 (4 s, 12 H, 4 AcO); $J_{3,4}$ 3.4, $J_{2,3}$ 11.3, $J_{1,2}$ 10.6, $J_{2,7}$ 1.7, $J_{3',5'}$ 2.1, $J_{5',6'}$ 8.3 Hz; ^{13}C, δ 169.5, 169.4, 169.7, and 167.7 (4 s, CH_3CO), 136.7 (s, C-1″), 135.3 (s, C-1′), 132.5 and 130.8 (2 s, C-2′,4′), 128.5 and 128.2 (2 d, C-3′,6′), 127.7 (d, C-3″), 126.9 (d, C-2″), 125.7 and 125.5 (2 d, C-5′,4″), 80.0 (d, C-1), 73.0, 68.8, 67.5, and 65.5 (4 d, C-3,4,5,7), 61.2 (t, C-6), 42.0 (d, C-2), 19.9, 19.7, 19.6, and 19.5 (4 q, 4 $COCH_3$).

Concentration of the fraction with R_F 0.2 and treatment of the residue with ether–hexane gave 2-*C*-[(*R*)-acetoxy(2,4-dichlorophenyl)methyl]-3,4,6-tri-*O*-acetyl-2-deoxy-β-L-*gulo*-hexopyranosylbenzene (**4**); 95 mg, 16%), mp 164–165°. ^{1}H-NMR

data: δ 7.23 (m, 5 H, Ph), 7.11 (d, 1 H, H-3), 7.00 (dd, 1 H, H-5′), 6.85 (d, 1 H, H-6′), 5.70 (d, 1 H, H-7), 5.13 (dd, 1 H, H-3), 4.97 (dd, 1 H, H-4), 4.84 (d, 1 H, H-1), 4.25–4.10 (m, 2 H, H-5,6a), 4.01 (dd, 1 H, H-6b), 3.01 (ddd, 1 H, H-2), 2.24, 2.15, 2.04, and 2.01 (4 s, 12 H, 4 AcO); $J_{6a,6b}$ 11.1, $J_{6b,2}$ 6.8, $J_{4,5}$ 1.3, $J_{3,4}$ 3.9, $J_{2,3}$ 2.5, $J_{1,2}$ 10.3, $J_{2,7}$ 6.8, $J_{3',5'}$ 2.1, $J_{5',6'}$ 8.3 Hz.

Anal. Calcd for $C_{27}H_{28}Cl_2O_9$: C, 57.15; H, 4.97; Cl, 12.50. Found for **4**: C, 57.12; H, 5.02; Cl, 12.43. Found for **6**: C, 57.21; H, 4.93; Cl, 12.48.

Deacetylation of **4** *and* **6**.—Treatment of **4** (80 mg) in MeOH (5 mL) with methanolic M sodium methoxide (0.01 mL) for 2 days at room temperature, then removal of the sodium ions with Varion KS (H^+) resin, and concentration, gave amorphous 2-deoxy-2-*C*-[(*R*)-(2,4-dichlorophenyl)hydroxymethyl]-β-L-*gulo*-hexopyranosylbenzene (**5**; 48 mg, 84%), R_F 0.5 (solvent *F*), ^{1}H-NMR data (pyridine-d_5): δ 8.04 (d, 1 H, H-6′), 7.92 (dd, 1 H, H-5′), 7.5–7.3 (m, 6 H, Ph and H-3′), 5.67 (d, 1 H, H-1), 5.20 (d, 1 H, H-7), 4.85 (td, 1 H, H-5), 4.49 (dd, 1 H, H-6a), 4.45–4.40 (m, 2 H, H-3,6b), 4.38 (dd, 1 H, H-4), and 3.10 (dt, 1 H, H-2); $J_{4,5}$ 1.1, $J_{3,4}$ 3.9, $J_{2,3}$ 2.4, $J_{2,7}$ 2.3, $J_{1,2}$ 10.6, $J_{6a,6b}$ 11.3, $J_{5,6a}$ 6.1 Hz.

Likewise, **6** (80 mg) gave 2-deoxy-2-*C*-[(*R*)-(2,4-dichlorophenyl)hydroxymethyl]-β-L-*galacto*-hexopyranosylbenzene (**7**; 45 mg, 78%), R_F 0.4 (solvent *F*). ^{1}H-NMR data (pyridine-d_5): δ 8.38 (d, 1 H, H-6′), 7.88 (dd, 1 H, H-5′), 7.50–7.25 (m, 5 H, Ph), 7.08 (d, 1 H, H-3′), 5.20 (d, 1 H, H-7), 5.14 (d, 1 H, H-1), 4.94 (dd, 1 H, H-3), 4.47 (d, 1 H, H-4), 4.45 (dd, 1 H, H-6a), 4.37 (dd, 1 H, H-6b), 4.17 (dd, 1 H, H-5), and 3.23 (td, 1 H, H-2); $J_{3,4}$ 3.1, $J_{2,3}$ 10.5, $J_{1,2}$ 10.2, $J_{2,7}$ 1.8, $J_{5,6a}$ 6.6, $J_{5,6b}$ 5.3, $J_{6a,6b}$ 11.3, $J_{3',5'}$ 2.0, $J_{5',6'}$ 8.0 Hz.

Anal. Calcd for $C_{19}H_{20}Cl_2O_5$: C, 57.15; H, 5.04; Cl, 17.75. Found for **5**: C, 57.11; H, 5.12; Cl, 17.58. Found for **7**: C, 57.15; H, 5.08; Cl, 17.61.

(E)-*5,6-Dideoxy-6*-C-*(2,4-dichlorophenyl)*-D-xylo-*hex-5-enitol* (**9**).—A solution of **8** (0.3 g) in MeOH (5 mL) and methanolic M sodium methoxide (0.1 mL) was stored for 2 days at room temperature, then neutralised with solid CO_2, and concentrated. Column chromatography (solvent *F*) of the residue gave **9** (0.14 g, 73.7%), isolated as syrup, R_F 0.3, $[\alpha]_D$ +18° (MeOH). ^{1}H-NMR data (Me_2SO-d_6): δ 7.67 (d, 1 H, H-6′), 7.52 (d, 1 H, H-3′), 7.37 (dd, 1 H, H-5′), 6.88 (d, 1 H, H-6), 6.57 (dd, 1 H, H-5), 4.25 (dd, 1 H, H-4), 3.77 t, 1 H, H-3), 3.7–3.3 (m, 3 H, H-1a,1b,2); $J_{2,3}$ 6.5, $J_{3,4}$ 6.5, $J_{4,5}$ 5.2, $J_{5,6}$ 15.9, $^4J_{3',5'}$ 2.0, $J_{5',6'}$ 8.5 Hz.

Anal. Calcd for $C_{12}H_{14}Cl_2O_4$: C, 49.16; H, 4.81; Cl, 24.19. Found: C, 49.10; H, 4.72; Cl, 24.05.

(Z)-*1,3-Di*-O-*acetyl-2,4*-O-*benzylidene-5,6-dideoxy-6*-O-*(pyrid-3-yl)*-D-xylo-*hex-5-enitol* (**11**).—To a stirred slurry of triphenyl (pyrid-3-ylmethyl)phosphonium chloride (2.9 g) in tetrahydrofuran (50 mL) and *N*,*N*-dimethylformamide (10 mL) was added potassium *tert*-butoxide (1.1 g). The orange solution was stirred for 1 h at room temperature, when crude 2,4-*O*-benzylidene-L-xylose [1] (**10**, 1.9 g) was added. After 30 min, the mixture was diluted with water (100 mL) and extracted with EtOAc, and the extract was washed with brine, dried, and concentrated. The residue was dissolved in pyridine (20 mL) and acetic anhydride (10 mL) was added.

After 20 h, the solution was concentrated, and toluene was evaporated from the residue. Column chromatography (solvent *A*) then gave **11** (1.47 g, 46.5%), R_F 0.5. ^{1}H-NMR data: δ 8.65–8.5 (m, 2 H, aromatic), 7.7–7.2 (m, 7 H, aromatic), 6.70 (d, 1 H, H-6), 5.82 (dd, 1 H, H-5), 5.70 (s, 1 H, PhC*H*), 5.08 (s, 1 H, H-3), 4.77 (d, 1 H, H-4), 4.35–4.05 (m, 3 H, H-1a,1b,2), 2.20 and 2.03 (2 s, 6 H, CMe_2); $J_{4,5}$ 8.6 and $J_{5,6}$ 11.7 Hz.

Anal. Calcd for $C_{22}H_{23}NO_6$: C, 66.48; H, 5.83; N, 3.52. Found: C, 66.36; H, 5.92; N, 3.30.

(Z)- (**12**) *and* (E)-*1,3-Di*-O-*acetyl-2,4*-O-*benzylidene-5,6-dideoxy-6*-C-*(4-nitrophenyl)*-D-xylo-*hex-5-enitol* (**15**).—(4-Nitrophenylmethyl)triphenylphosphonium chloride (4.8 g), potassium *tert*-butoxide (1.3 g), and **10** (2.4 g) were reacted, as described for **11**. Column chromatography (solvent *C*) of the product gave, first, **12** (1.5 g, 34%), mp 118–120° (from ether–hexane), $[\alpha]_D$ +127°, R_F 0.5. ^{1}H-NMR data: δ 8.23 (d, 2 H, aromatic), 7.55–7.35 (m, 7 H, aromatic), 6.78 (d, 1 H, H-6), 5.85 (dd, 1 H, H-5), 5.69 (s, 1 H, PhC*H*), 5.07 (t, 1 H, H-3), 4.75 (dd, 1 H, H-4), 4.35–4.10 (m, 1 H, H-1a,1b,2), 2.23 and 2.05 (2 s, 6 H, CMe_2); $J_{2,3}$ 1.4, $J_{3,4}$ 1.4, $J_{4,5}$ 8.4, $J_{5,6}$ 11.9 Hz.

Eluted second was **15** (0.5 g, 11.4%), mp 130–132° (from ether–hexane), $[\alpha]_D$ −46°, R_F 0.4. ^{1}H-NMR data: δ 8.17 (d, 2 H, aromatic), 7.65–7.30 (m, 7 H, aromatic), 6.84 (dd, 1 H, H-6), 6.29 (dd, 1 H, H-5), 5.79 (s, 1 H, PhC*H*), 5.18 (t, 1 H, H-3), 4.82 (dt, 1 H, H-4), 4.40 (m, 1 H, H-2), 4.25 (m, 2 H, H-1a,1b), 2.08 and 2.05 (2 s, 6 H, CMe_2); $J_{2,3}$ 1.6, $J_{3,4}$ 1.6, $J_{4,5}$ 4.3, $J_{5,6}$ 16.0, $J_{4,6}$ 1.5 Hz.

Anal. Calcd for $C_{23}H_{23}NO_8$: C, 62.57; H, 5.25; N, 3.17. Found for **12**: C, 62.52, H, 5.22; N, 3.05. Found for **15**: C, 62.49; H, 5.34; N, 3.11.

(Z)- (**13**) *and* (E)-1,3-*Di*-O-*acetyl-2,4*-O-*benzylidene-5,6-dideoxy-6*-C-*(2-nitrophenyl)*-D-xylo-*hex-5-enitol* (**16**).—(2-Nitrophenylmethyl)triphenylphosphonium chloride (4.34 g), potassium *tert*-butoxide (1.3 g), and **10** (2.4 g) were reacted, as described for **11**. Column chromatography (solvent *B*) of the product gave, first, **13** (2.12 g, 48%), mp 90–92° (from ether–hexane), $[\alpha]_D$ +34°, R_F 0.5. ^{1}H-NMR data: δ 8.03 (dd, 1 H, aromatic), 7.65–7.25 (m, 8 H, aromatic), 6.99 (d, 1 H, H-6), 5.81 (dd, 1 H, H-5), 5.55 (s, 1 H, PhC*H*), 5.00 (s, 1 H, H-3), 4.58 (d, 1 H, H-4), 4.25–4.0 (m, 3 H, H-1a,1b,2), 2.18 and 2.01 (2 s, 6 H, CMe_2); $J_{4,5}$ 7.8 and $J_{5,6}$ 11.8 Hz.

Eluted second was **16** (0.96 g, 21%), isolated as a syrup, $[\alpha]_D$ +21°, R_F 0.4. ^{1}H-NMR data: δ 7.94 (dd, 1 H, aromatic), 7.65–7.35 (m, 8 H, aromatic), 7.26 (dd, 1 H, H-6), 6.09 (dd, 1 H, H-5), 5.78 (s, 1 H, PhC*H*), 5.17 (t, 1 H, H-3), 4.80 (dt, 1 H, H-4), 4.45–4.05 (m, 3 H, H-1a,1b,2), 2.12 and 2.09 (2 s, 6 H, CMe_2); $J_{2,3}$ 1.5, $J_{3,4}$ 1.5, $J_{4,5}$ 4.7, $J_{5,6}$ 15.8, $^4J_{4,6}$ 1.3 Hz.

Anal. Calcd for $C_{23}H_{23}NO_8$: C, 62.57; H, 5.25; N, 3.17. Found for **13**: C, 62.53; H, 5.18; N, 3.15. Found for **14**: C, 62.43; H, 5.34; N, 3.03.

Acetolysis of (Z)-*2,4*-O-*benzylidene-1,3-di*-O-p-*toluenesulfonyl-5,6-dideoxy-6*-C-*(2,4-dichlorophenyl)*-D-xylo-*hex-5-enitol* [1] (**17**).—Acetolysis of **17** (2 g), as described for **3**, gave products with R_F 0.8, 0.7, and 0.3 (TLC, solvent *C*).

Column chromatography (solvent *D*) gave, first, 2-deoxy-2-*C*-[(*R*)-(2,4-dichlorophenyl)hydroxymethyl]-4,6-di-*O*-*p*-toluenesulfonyl-β-L-*galacto*-hexopyranosylbenzene 3,7-(cyclic sulfate) (**18**; 30 mg, 2.7%), isolated as syrup, R_F 0.8 (solvent *C*). NMR data (benzene-d_6): ^{1}H, δ 7.97, 7.75, and 6.94 (3 d, 6 H, aromatic), 6.8–6.5 (m, 8 H, aromatic), 6.28 (dd, 1 H, H-5′), 5.95 (d, 1 H, H-6′), 6.11 (d, 1 H, H-7), 5.11 (d, 1 H, H-4), 4.90 (dd, 1 H, H-3), 4.60 (dd, 1 H, H-6a), 4.38 (dd, 1 H, H-6b), 3.88 (d, 1 H, H-5), 3.82 (d, 1 H, H-1), 2.93 (q, 1 H, H-2), 1.93 and 1.81 (2 s, 6 H, 2 Ts*Me*); $J_{6a,6b}$ 11.0, $J_{6a,5}$ 4.8, $J_{6b,5}$ 7.0, $J_{3,4}$ 2.8, $J_{2,3}$ 10.9, $J_{1,2}$ 10.2, $J_{2,7}$ 10.9, $J_{3',5'}$ 2.1, $J_{5',6'}$ 8.3 Hz; ^{13}C, δ 145.9 (s), 145.0 (s), 136.1 (s), 135.3 (s), 133.9 (s), 132.6 (s), 132.2 (s), 130.2 (d), 130.0 (d), 129.8 (d), 129.7 (s), 128.9 (d), 128.7 (d), 128.2 (d), 128.0 (d), 127.5 (d), 127.3 (d), 82.6 (d), 82.2 (d), 78.9 (d), 74.9 (d), 73.5 (d), 67.9 (t), 43.2 (d), 21.7 (q), and 21.6 (q).

Anal. Calcd for $C_{33}H_{30}Cl_2O_{11}S_3$: C, 51.59; H, 3.92; S, 12.49. Found: C, 51.41; H, 4.05; S, 12.33.

The fractions with R_F 0.7 and 0.3 were mixtures (NMR data) of products with no phenyl substituents.

*2,4-O-Benzylidene-3-O-methyl-*L*-xylose* (**20**).—A solution of $NaIO_4$ (0.6 g) in water (1.8 mL) was added to a slurry of 2,4-*O*-benzylidene-3-*O*-methyl-D-glucitol [5] (**19**, 0.8 g) and $NaHCO_3$ (0.1 g) in dioxane (8 mL). After 1.5 h, the inorganic salts were collected and washed with EtOH, and the filtrate and washings were combined and concentrated. The residue was extracted with EtOH, and the extract was concentrated and then diluted with ether to give **20** (0.6 g, 84.5%), mp 78–90°, R_F 0.6 (solvent *A*). According to the small intensity of the ^{1}H signal at δ 9.62 and ^{13}C signal at δ 200.5, the free aldehyde was present only as a minor component in the mixture in which the hydrate and ethyl hemiacetal preponderated.

A solution of **20** (150 mg) and 4-nitrophenylhydrazine (100 mg) in MeOH (10 mL) was boiled under reflux for 15 min, then concentrated. Column chromatography (solvent *A*) of the residue gave 2,4-*O*-benzylidene-3-*O*-methyl-L-xylose 4-nitrophenylhydrazone (210 mg, 91%), mp 168–170° (from ether), R_F 0.7 (solvent *A*). ^{1}H-NMR data: δ 11.10 (s, 1 H, NH), 8.12 (d, 2 H, H-3′,5′), 7.5–7.3 (m, 6 H, aromatic and H-5), 7.05 (d, 2 H, H-2′,6′), 5.75 (s, 1 H, PhC*H*), 4.70 (d, 1 H, H-4), 4.05 m, 1 H, H-2), 3.60 (m, 2 H, H-1a,1b), 3.44 (s, 1 H, H-3), and 3.42 (s, 3 H, MeO); $J_{4,5}$ 5.9 and $J_{2',3'}$ 9.3 Hz.

Anal. Calcd for $C_{19}H_{21}N_3O_6$: C, 58.90, H, 5.46; N, 10.84. Found: C, 58.76; H, 5.55; N, 10.98.

*(Z)-2,4-O-Benzylidene-5,6-dideoxy-6-C-(2,4-dichlorophenyl)-3-O-methyl-*D*-xylo-hex-5-enitol* (**21**).—Potassium *tert*-butoxide (0.25 g) was added to a stirred slurry of (2,4-dichlorophenylmethyl)triphenylphosphonium chloride in tetrahydrofuran (5 mL) and *N*,*N*-dimethylformamide (5 mL). After 1 h, **20** (0.43 g) was added to the orange solution. After 30 min, the mixture was diluted with water and extracted with EtOAc, and the extract was washed with brine, dried, and concentrated. Column chromatography (solvent *B*) of the residue gave **21** (0.28 g, 42%), mp 180–182° (from ether–hexane). $[\alpha]_D$ +216°, R_F 0.4. ^{1}H-NMR data: δ 7.55–7.20

(m, 9 H, aromatic), 6.75 (d, 1 H, H-6), 6.19 (dd, 1 H, H-5), 6.15 (s, 1 H, PhC*H*), 4.51 (d, 1 H, H-4), 4.05–3.75 (m, 3 H, H-1a,1b,2), 3.58 (s, 3 H, MeO), 3.12 (s, 1 H, H-3), and 2.03 (bs, 1 H, OH); $J_{4,5}$ 8.9 and $J_{5,6}$ 11.6 Hz.

Anal. Calcd for $C_{20}H_{20}Cl_2O_4$: C, 60.76; H, 5.10; Cl, 17.94. Found: C, 60.72; H, 5.03; Cl, 17.88.

The presence of the corresponding 5*E* isomer could not be detected by NMR spectroscopy in any of the fractions.

(Z)-*1*-O-*Acetyl-2,4*-O-*benzylidene-5,6-dideoxy-6*-C-*(2,4-dichlorophenyl)-3*-O-*methyl*-D-xylo-*hex-5-enitol* (**22**).—Acetic anhydride (2 mL) was added to a stirred slurry of **21** (1.7 g) in pyridine (5 mL); **22** started to separate after 15 min. After 20 h, the mixture was poured into water, and the precipitate was collected and washed with water to give **22** (1.8 g, 95%), mp 161–163°, $[\alpha]_D$ +173°, R_F 0.7 (solvent *D*). ^{1}H-NMR data: δ 7.7–7.2 (m, 8 H, aromatic), 6.76 (d, 1 H, H-6), 6.19 (dd, 1 H, H-5), 5.57 (s, 1 H, PhC*H*), 4.52 (d, 1 H, H-4), 4.33 (m, 2 H, H-1a,1b), 4.06 (m, 1 H, H-2), 3.59 (s, 3 H, MeO), 3.10 (s, 1 H, H-3), and 2.08 (s, 3 H, AcO); $J_{4,5}$ 8.9 and $J_{5,6}$ 11.6 Hz.

Anal. Calcd for $C_{22}H_{22}Cl_2O_5$: C, 60.41; H, 5.07; Cl, 16.21. Found: C, 60.44; H, 5.00; Cl, 16.12.

Acetolysis of **22**.—Acetolysis of **22** (3 g), as described for **3**, gave a multicomponent mixture, column chromatography (solvent *B*) of which gave a fraction (0.8 g) with R_F 0.6. This solid product was extracted with ether (3 × 3 mL), which left a solid residue that contained (NMR data) **23** and **8** in the ratio 2:1.

Concentration of the combined extracts afforded 6-*O*-acetyl-2-deoxy-2-*C*-[(*R*)-(2,4-dichlorophenyl)hydroxymethyl]-4-*O*-methyl-β-L-*galacto*-hexopyranosylbenzene 3,7-(cyclic sulfate) (**25**; 70 mg, 2%), mp 110–112° (dec). NMR data: ^{1}H, δ 7.15–6.85 (m, 8 H, aromatic), 6.18 (d, 1 H, H-7), 5.14 (dd, 1 H, H-3), 4.3–4.2 (m, 3 H, H-1,6a,6b), 3.88 (m, 1 H, H-5), 3.82 (d, 1 H, H-4), 3.67 (s, 3 H, MeO), 3.29 (q, 1 H, H-2), and 2.06 (s, 3 H, AcO); $J_{1,4}$ 1.4, $J_{2,3}$ 10.9, $J_{1,2}$ 11.0, $J_{2,7}$ 11.2 Hz; ^{13}C, δ 170.5 (s), 135.9 (s), 133.9 (s), 130.4 (s), 130.3 (d), 128.9 (d), 128.6 (d), 128.0 (d), 127.6 (d), 127.3 (d), 86.5 (d), 83.0 (d), 79.4 (d), 75.9 (d), 75.1 (d), 62.5 (t), 61.7 (q), 42.9 (d), and 20.8 (q).

Anal. Calcd for $C_{22}H_{22}Cl_2O_8S$: C, 51.06; H, 4.28; Cl, 13.70; S, 6.19. Found: C, 50.92; H, 4.11, Cl, 13.55, S, 6.25.

Concentration of the fractions with R_F 0.5 gave 2-*C*-[(*R*)-acetoxy(2,4-dichlorophenyl)methyl]-3,6-di-*O*-acetyl-2-deoxy-4-*O*-methyl-β-L-*galacto*-hexopyranosylbenzene (**24**; 0.75 g, 20.3%), $[\alpha]_D$ −19°. ^{1}H-NMR data: δ 7.38 (m, 5 H, Ph), 7.27 (d, 1 H, H-3′), 7.12 (dd, 1 H, H-5′), 7.01 (d, 1 H, H-6′), 5.60 (d, 1 H, H-7), 5.43 (dd, 1 H, H-3), 4.37 (d, 1 H, H-1), 4.23 (m, 2 H, H-6a,6b), 3.79 (m, 1 H, H-5), 3.58 (d, 1 H, H-4), 3.41 (s, 3 H, MeO), 3.10 (td, 1 H, H-5), 2.23, 2.04, and 1.57 (3 s, 9 H, 3 AcO); $J_{3,4}$ 3.2, $J_{2,3}$ 11.3, $J_{1,2}$ 10.3, $J_{2,7}$ 1.1, $J_{3',5'}$ 2.0, and $J_{5',6'}$ 8.4 Hz.

Anal. Calcd for $C_{26}H_{28}Cl_2O_8$: C, 57.89; H, 5.23; Cl, 13.14. Found: C, 57.72; H, 5.33, Cl, 13.08.

2-Deoxy-2-C-[(R)-(2,4-dichlorophenyl)hydroxymethyl]-4-O-methyl-β-L-galacto-hexopyranosylbenzene (**26**).—To a solution of **24** (0.7 g) in MeOH (5 mL) and $CHCl_3$ (5 mL) was added methanolic M sodium methoxide (0.05 mL). The mixture was stored for 20 h at room temperature, then concentrated. Column chromatography (solvent *A*) of the residue gave amorphous **26** (215 mg, 40.1%), $[\alpha]_D$ −27°, R_F 0.5. NMR data: ^1H, δ 7.55–7.05 (m, 8 H, aromatic), 4.67 (d, 1 H, H-7), 4.40 (d, 1 H, H-1), 4.21 (dd, 1 H, H-3), 3.86 (dd, 1 H, H-6a), 3.7–3.5 (m, 2 H, H-5,6b), 3.45 (s, 3 H, MeO), 3.34 (d, 1 H, H-4), 2.61 and 1.98 (2 bs, 2 H, OH), 2.46 (td, 1 H, H-2); $J_{6a,6b}$ 10.8, $J_{6a,5}$ 7.6, $J_{3,4}$ 3.6, $J_{2,3}$ 10.3, $J_{1,2}$ 10.3, $J_{2,7}$ 2.7 Hz; ^{13}C, δ 140.5, 139.0 (C-1′, 1″), 132.9 (C-4′), 131.4 (C-2′), 129.6 (C-6′), 128.5 (C-4″), 128.4 and 128.2 (C-2″, 3″), 126.5 (C-5′), 81.2 (C-1), 79.4 and 79.2 (C-4,5), 69.8 (C-3), 68.9 (C-7), 62.6 (C-6), 61.8 (MeO), and 48.5 (C-2).

Anal. Calc. for $C_{20}H_{22}Cl_2O_5$: C, 58.12; H, 5.37; Cl, 17.15. Found: C, 58.03; H, 5.25; Cl, 17.00.

2-Deoxy-2-C-[(R)-(2,4-dichlorophenyl)hydroxymethyl]-3,7-O-isopropylidene-4-O-methyl-β-L-galacto-hexopyranosylbenzene (**27**).—To a solution of **26** (200 mg) in acetone (10 mL) were added 2-methoxypropene (0.2 mL) and then *p*-toluenesulfonic acid (0.01 g). After 2 days, when TLC indicated the reaction to be complete (R_F 0.5 → 0.85, solvent *A*), the solution was neutralised with solid $NaHCO_3$, filtered, and concentrated. Column chromatography (solvent *B*) of the residue gave **27** (130 mg, 59.4%), isolated as a syrup, $[\alpha]_D$ +60°, R_F 0.5. NMR data: ^1H, δ 7.11 (d, 1 H, H-6′), 7.0–6.9 (m, 5 H, Ph), 6.85 (dd, 1 H, H-5′), 6.79 (d, 1 H, H-3′), 5.24 (d, 1 H, H-7), 4.19 (dd, 1 H, H-3), 4.17 (d, 1 H, H-1), 3.86 (dd, 1 H, H-6a), 3.73 (ddd, 1 H, H-5), 3.67 (dd, 1 H, H-6b), 3.66 (s, 3 H, MeO), 3.52 (dd, 1 H, H-4), 2.74 (q, 1 H, H-2), 1.62 and 1.46 (2 s, 6 H, Me_2C); $J_{6a,6b}$ 11.4 , $J_{6a,5}$ 7.2, $J_{6b,5}$ 4.2, $J_{4,5}$ 1.2, $J_{3,4}$ 2.7, $J_{2,3}$ 10.8, $J_{1,2}$ 10.8, $J_{2,7}$ 10.8, $J_{3',5'}$ 2.0, $J_{5',6'}$ 8.2 Hz; ^{13}C, δ 137.8 (C-1″), 135.4 (C-1′), 133.6 and 133.4 (C-2′,4′), 130.7 (C-6′), 128.2 (C-3′), 127.9 (C-2″), 127.8 (C-4″), 127.7 (C-3″), 127.0 (C-5′), 99.6 (Ph*C*H), 80.3 (C-1), 79.3 (C-5), 76.8 (C-4), 75.7 (C-3), 68.9 (C-7), 63.1 (C-6), 61.2 (MeO), 30.1 (*ax*-CH_3C) and 19.5 (*eq*-CH_3C).

Anal. Calcd for $C_{23}H_{26}Cl_2O_5$: C, 60.93; H, 5.78; Cl, 15.64. Found: C, 60.77; H, 5.82; Cl, 15.51.

(Z)-1,2,3,4-Tetra-O-acetyl-5,6-dideoxy-6-C-(2,4-dichlorophenyl)-D-xylo-hex-5-enitol (**42**, $R^1 = R^2 =$ Ac).—A solution of **2** (0.4 g) in pyridine (5 mL) and acetic anhydride (3 mL) was kept at room temperature for 4 h to give, after the usual processing, **42** (0.6 g, 95%), as a syrup, $[\alpha]_D$ +104°, R_F 0.35 (solvent *D*). ^1H-NMR data: δ 7.62 (d, 1 H, H-6′), 7.43 (d, 1 H, H-3′), 7.27 (dd, 1 H, H-5′), 6.71 (d, 1 H, H-6), 5.80 (dd, 1 H, H-4), 5.68 (dd, 1 H, H-5), 5.31 (dd, 1 H, H-3), 5.15 (q, 1 H, H-2), 4.23 (dd, 1 H, H-1a), 3.89 (dd, 1 H, H-1b), 2.08, 2.07, 2.00, and 1.78 (4 s, 12 H, 4 AcO); $J_{1a,1b}$ 11.8, $J_{1a,2}$ 5.4, $J_{1b,2}$ 5.7, $J_{2,3}$ 4.7, $J_{3,4}$ 6.3, $J_{4,5}$ 9.8, $J_{5,6}$ 11.4, $J_{3',5'}$ 2.1, $J_{5',6'}$ 8.3 Hz.

Anal. Calcd for $C_{20}H_{22}Cl_2O_8$: C, 52.07; H, 4.80; Cl, 15.37. Found: C, 52.15; H, 5.03; Cl, 15.02.

Acetolysis of **42** (0.5 g), as described for **3**, gave a product (0.45 g, 90%), the ^{1}H-NMR spectrum of which contained signals for H-5, corresponding to the 5*E* (**8**) and 5*Z* (**42**) isomers at δ 6.05 and 5.68, respectively, in the ratio 1:2.

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