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STEREOSELECTIVE ARYLATION OF PYRANOID GLYCALS, USING BROMOMAGNESIUM PHENOLATES: AN ENTRY TO 2,3-UNSATURATED *C*-α-GLYCOPYRANOSYLARENES

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ABSTRACT

The arylation of acetylated pyranoid glycals at C-1 by means of bromomagnesium phenolates provides a highly stereoselective entry to 1-*C*-α-glycopyranosyl-2-hydroxyarenes.

INTRODUCTION

The alkylation of acetylated glycals at C-1 by carbon nucleophiles (the carbon version of the Ferrier rearrangement[1]) is a route to 2,3-unsaturated *C*-glycosyl derivatives. Regio- and stereo-selective processes have been exploited that involve various nucleophiles, including allylsilanes[2], silyl enol ethers[3] and homoenolate-equivalents[4], ene[5] and cyano[6] reagents, malonate and related anions[7], and organoaluminium compounds[8].

We now report on the use of metal phenolates for the arylation of pyranoid glycals[9] in order to obtain 2,3-unsaturated *C*-glycopyranosylarenes, a structure closely related to a significant group of natural products[10].

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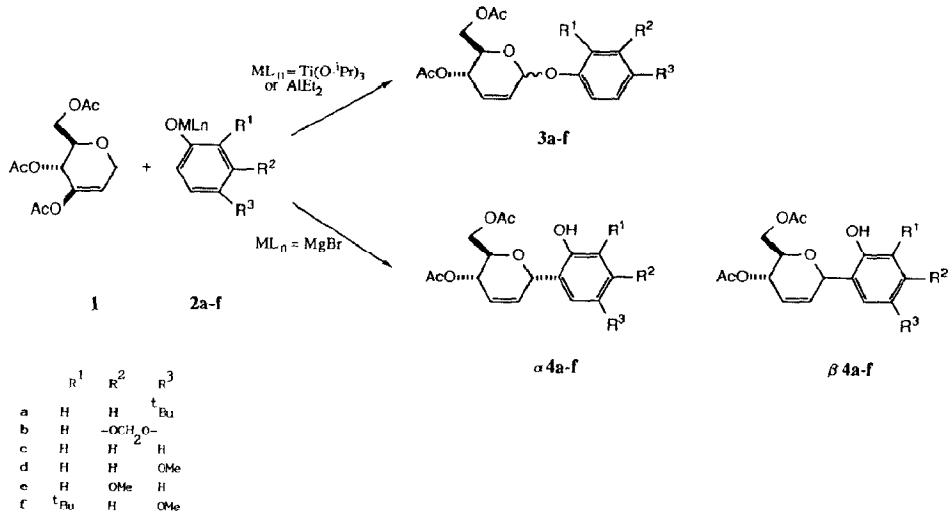
RESULTS AND DISCUSSION

Arylation procedure. — The phenolates of certain co-ordinating metals are Lewis acids and also possess an activated nucleophilic ring with one reactive *ortho*-carbon[11]. When applied to chiral carbonyl electrophiles, these reagents serve both as metal promoters and arylation reagents affording chiral arylated derivatives stereo- and regio-selectively[12].

The reactions between the titanium, aluminium, and magnesium salts of 4-*tert*-butylphenol [**2a**, ML_n = $Ti(O\text{-}i\text{-}Pr)_3$, $AlEt_2$, and MgBr] and 3,4,6-tri-*O*-acetyl-D-glucal (**1**) in aprotic non-polar solvents was investigated first. Whereas the tri-isopropoxytitanium salt in toluene at ambient temperature gave Ferrier-type *O*-substitution products **3** exclusively ($\alpha\beta$-ratio 20:1), as did the diethylaluminium phenolate, the bromomagnesium salt of **2a** reacted sluggishly with **1** in dichloromethane (15% reaction after 56 h at ambient temperature), affording the axial *C*-glycosylarene α**4a** as the sole stereoisomer in 12% yield. This behaviour is attributed to the heterogeneous nature of the reaction mixture or to unproductive aggregation phenomena involving the bromomagnesium phenolate and the oxygen ligand groups of **1**[13].



	R^1	R^2	R^3
a	H	H	^{t}Bu
b	H	$-OCH_2O-$	
c	H	H	H
d	H	H	OMe
e	H	OMe	H
f	^{t}Bu	H	OMe

For successful arylation, it was necessary to use 4 mol of the bromomagnesium salt of **2a** combined with ultrasonic irradiation[14]. When the reaction was carried out under these conditions in dichloromethane at ambient temperature, the α-glycoside α**4a** was obtained (71% yield) and the β anomer was not detected.

This modification was effective in each of the reactions since bromomagnesium phenolates self-aggregate easily in dichloromethane, producing inert slurries, and ultrasound is energetic enough to destroy the molecular aggregates, thereby enhancing the reaction rate significantly. Thus, by using this improved

TABLE I

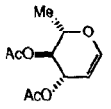
SYNTHESIS OF C-α- AND -β-GLYCOSYLARENES

Phenol	*Glycal*	*Products*	*Combined yield (%)*	*αβ-Ratio*[a]
2a	1	**α4a**	71	>100:1
2b	1	**α4b** + **β4b**	80	27:1
2c	1	**α4c** + **β4c**	63	26:1
2d	1	**α4d**	82	>100:1
2e	1	**α4e** + **β4e**	69	21:1
2f	1	**α4f**[b]	66	60:1
2b	5	**α6** + **β6**	77	8:1
2b	7	**α8**	12	>100:1

[a]Determined by reverse-phase h.p.l.c. [b]α Anomer not isolated.

procedure and the variously substituted bromomagnesium phenolates **2a–f**, several aromatic groups were introduced axially at C-1 of the glucal derivative **1** to give the unsaturated α-*C*-glucosylarenes **α4a–f** as the preponderant or exclusive products (Table I). Where present, the minor β anomers were isolated easily by chromatography.

The *C*-glycosylation procedure was then applied to the commercially available glycals, 2,4-di-*O*-acetyl-L-rhamnal (**5**) and 3,4,6-tri-*O*-acetyl-D-galactal (**7**).



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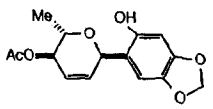
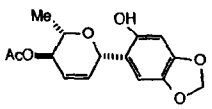
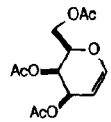


α6



β6



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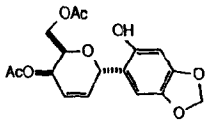

α8

The reaction between the bromomagnesium salt of **2b** and **5** gave the α- (**α6**) and β-L-glycosylarenes (**β6**) with an αβ-ratio of 8:1 (Table I). However, the reactivity of the galactal derivative **7**, even with the activated phenol **2b** (Table I), was low and, although the stereoselectivity was excellent (αβ-ratio >100:1), the yield of the isolated α-galactosylarene **8** was only 12%. The yield was increased only slightly (15%) on raising the reaction temperature from 20° to 50°.

TABLE II

DIAGNOSTIC DATA FOR *C*-α- AND -β-GLYCOSYLARENES

Compound	$[\alpha]_D^{20}$[a] *(degrees)*	*δ values (p.p.m.)*			$J_{1,2}$ *(Hz)*	$J_{4,5}$ *(Hz)*	*N.O.e. (%)*[b]	*Configuration*
		H-2	*H-3*	*H-4*				
α4a	+58	6.28	6.05	5.23	2.89	6.92	−	α-D
α4b	−24	6.21	6.02	5.26	3.22	7.14	−	α-D
β4b	+187	5.94	5.86	5.47	1.60	8.95	+	β-D
α4c	+77	6.27	6.03	5.25	3.04	6.60	−	α-D
β4c	+191	5.91	5.82	5.40	1.27	9.21	+	β-D
α4d	+34	6.27	6.04	5.25	3.11	6.56	−	α-D
α4e	+78	6.26	6.00	5.25	3.11	7.12	−	α-D
β4e	+174	5.88	5.73	5.38	1.81	9.12	+	β-D
α4f	+53	6.31	6.00	5.23	3.03	7.01	−	α-D
α6	+25	6.09	5.98	5.01	2.69	4.58	−	α-L
β6	−270	5.91	5.89	5.22	1.66	8.89	+	β-L
α8	+18	6.42	6.22	5.10	3.76	2.69	−	α-D

[a]In chloroform (*c* 1). [b]Enhancement of H-1 signal upon irradiation of H-5: +, strong n.O.e.; −, no effect.

Configurational assignment. — The stereochemistry at C-1 of 2,3-unsaturated *C*-glucopyranosyl derivatives can be assigned mainly on the basis of ^{1}H-n.m.r. and optical rotation measurements[15]. Thus, for a given pair of anomers (**α4** and **β4**) in the D series, the more dextrorotatory member with a n.O.e. between H-1 and H-5 was assigned as β. The values of $J_{1,2}$ and $J_{4,5}$ were also diagnostic, the respective values being 1.2–1.8 and 8.9–9.2 Hz for the β anomers and 2.9–3.8 and 4.5–7.1 Hz for the α anomers (Table II).

This simple rule applies also to the anomeric L-rhamnosylarenes **α6** and **β6** (in the L series, the more levorotatory member is β-L). The D-galactosylarene **8** was designated as α by analogy with the corresponding D-glucosylarene **α4b**.

X-Ray studies. — Discrepancies in the literature and misassignment of anomeric configuration to 2,3-unsaturated *C*-glycosylarenes[16,17] prompted an X-ray analysis of **β4b**. Fig. 1 shows an ORTEP drawing of the molecule with the atomic numbering scheme.

The enopyranosyl ring is in the half-chair conformation[18], with the three substituents equatorial [puckering parameters: q_2 = 0.39(1) Å, q_3 = 0.29(1) Å, Φ_2 = −22(2)°, Q = 0.490(11) Å, Θ_2 = 53(1)°; torsion angles: C-11–C-1–O-1–C-5 −167(1)°, C-6–C-5–C-4–C-3 −164(1)°, O-5–C-4–C-5–O-1 −162(1)°]. For the dioxalane ring, the Φ_2 value (108°) corresponds to an envelope conformation with C_s symmetry (mirror plane through vertex C-17)[19], the benzene ring is planar, and the phenolic oxygen atom lies on the same plane. An intramolecular hydrogen bond HO-4···O-1 = 2.602(11) Å is present so that the packing of the molecules is entirely due to Van der Waals forces. The H-1–H-5 bond distance (2.47 Å) accounts for the considerable n.O.e. effect observed in solution. The distances

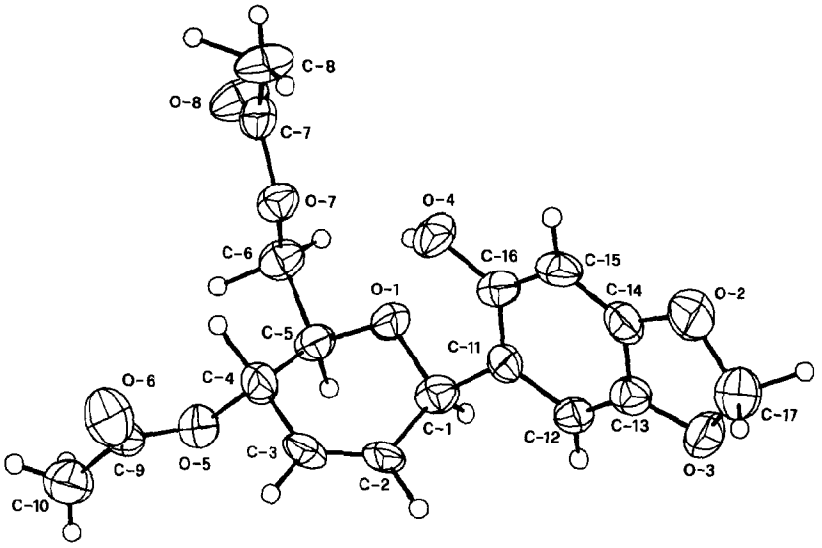

Fig. 1. The crystal structure of 1-(4,6-di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl)-2-hydroxy-4,5-methylenedioxybenzene (**β4b**) showing the atomic numbering scheme. Thermal ellipsoids enclose 50% of probability, and the hydrogen atoms are drawn with an arbitrary diameter.

between all non-hydrogen atoms are normal. Some selected distances and torsion angles are reported: C-1–O-1 1.45(1), C-5–O-1 1.42(1), C-4–C-5 1.54(2), C-3–C-4 1.49(2), C-2–C-3 1.31(1), C-1–C-2 1.49(1), C-16–O-4 1.37(1) Å; C-2–C-1–C-11–C-16 −92(1), O-1–C-5–C-6–O-7 −56(1), C-5–C-4–O-5–C-9 −154(1), C-15–C-14–C-13–O-3 177(1), O-4–C-16–C-11–C-1 −6(2)°.

The high regio- and stereo-selectivity of the reactions reported is noteworthy, with the α anomer being produced preponderantly or exclusively, which suggests that the *ortho*-carbon of the aromatic ring of bromomagnesium phenolates is a reactive nucleophile that reacts preferentially from the axial direction at C-1 and anti to the 3- and 5-substituents according to a S_N2' anti-selective process.

The reaction is sensitive to the disposition of the acetoxyl group adjacent to the leaving group in the 3-position, which precludes application to sugars having a 3,4-*cis* relationship (*e.g.*, galactal derivatives)[20].

EXPERIMENTAL

General. — ^{1}H-N.m.r. spectra were recorded at 270 MHz and 22 ±1° for solutions in $CDCl_3$ (internal Me_4Si). $[\alpha]_D$ values were determined on a Perkin–Elmer 241 polarimeter. Melting points were determined on a Buchi 510 apparatus and are uncorrected.

Flash chromatography[21] was performed on Silica Gel 60 (Merck, 0.040–0.063

mm), and t.l.c. on Silica Gel 60 F_{254} (Merck) with detection by ethanolic 7% phosphomolybdic acid. Dichloromethane was distilled from calcium hydride and stored over 4-Å molecular sieves.

3,4,6-Tri-*O*-acetyl-D-glucal (Janssen), 3,4-di-*O*-acetyl-L-rhamnal (Fluka), 3,4,6-tri-*O*-acetyl-D-galactal (Merck), and all the phenols were commercial products.

Sonicated reactions were carried out with a Branson Model B-3200E2 ultrasonic cleaner, with the raction vessels completely submerged in a water bath at the appropriate temperature.

Reaction of bromomagnesium phenolates with acetylated glycals. — To a solution of ethylmagnesium bromide prepared from ethyl bromide (4.32 g, 40 mmol) and magnesium turnings (0.96 g) in ether (150 mL) was added dropwise a solution of the appropriate phenol (40 mmol) in ether (150 mL) with stirring at room temperature. The ether was removed under vacuum, and anhydrous CH_2Cl_2 (100 mL) was added. The reaction vessel was placed in an ice-cooled sonication bath and a solution of the acetylated glycal (10 mmol) in CH_2Cl_2 (50 mL) was added dropwise. After 6 h at 22°, the mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (3 × 50 mL), and the combined extracts were dried and concentrated under reduced pressure. Flash chromatography (hexane–ethyl acetate mixtures) of the residue gave, first the *β-C*-glycosylarene (if present) and then the *α* anomer.

The following compounds were prepared in this manner. The yields and *αβ*-ratios are recorded in Table I, and the $[\alpha]_D$ values in Table II.

5-*tert*-Butyl-1-(4,6-di-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranosyl)-2-hydroxybenzene (***α*4a** from **1** and **2a**) isolated as an oil. ^{1}H-N.m.r. data: δ 1.28 (s, 9 H, ^{t}Bu), 2.09 and 2.11 (2 s, each 3 H, 2 Ac), 4.02 (ddd, 1 H, $J_{4,5}$ 6.92, $J_{5,6a}$ 6.23, $J_{5,6b}$ 4.15 Hz, H-5), 4.21 (dd, 1 H, $J_{6a,6b}$ 11.81 Hz, H-6b), 4.26 (dd, 1 H, H-6a), 5.23 (m, 1 H, H-4), 5.47 (m, 1 H, H-1), 6.05 (ddd, 1 H, $J_{2,3}$ 10.28, $J_{3,4}$ 3.53, $J_{1,3}$ 1.92 Hz, H-3), 6.28 (ddd, 1 H, $J_{1,2}$ 2.89, $J_{2,4}$ 1.28 Hz, H-2), 6.85 (d, 1 H, $J_{3',4'}$ 8.35 Hz, H-3'), 7.04 (d, 1 H, $J_{4',6'}$ 2.57 Hz, H-6'), 7.09 (s, 1 H, OH), 7.27 (dd, 1 H, H-4').

Anal. Calc. for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 66.31; H, 7.30.

1-(4,6-Di-*O*-acetyl-2,3-dideoxy-*α*-D-*erythro*-hex-2-enopyranosyl)-2-hydroxy-4,5-methylenedioxybenzene (***α*4b** from **1** and **2b**), m.p. 126–128°. ^{1}H-N.m.r. data: δ 2.08 and 2.09 (2 s, each 3 H, 2 Ac), 3.91 (ddd, 1 H, $J_{4,5}$ 7.14, $J_{5,6a}$ 6.50, $J_{5,6b}$ 3.51 Hz, H-5), 4.19 (dd, 1 H, $J_{6a,6b}$ 12.05 Hz, H-6b), 4.22 (dd, 1 H, H-6a), 5.26 (dm, 1 H, H-4), 5.43 (m, 1 H, H-1), 5.91 (s, 2 H, OCH_2O), 6.02 (ddd, 1 H, $J_{2,3}$ 10.47, $J_{3,4}$ 2.65, $J_{1,3}$ 2.06 Hz, H-3), 6.21 (ddd, 1 H, $J_{1,2}$ 3.22, $J_{2,4}$ 1.02 Hz, H-2), 6.50 (s, 1 H, H-3'), 6.57 (s, 1 H, H-6'), 7.02 (s, 1 H, OH).

Anal. Calc. for $C_{17}H_{18}O_8$: C, 58.28; H, 5.18. Found: C, 58.41; H, 5.40.

1-(4,6-Di-*O*-acetyl-2,3-dideoxy-*β*-D-*erythro*-hex-2-enopyranosyl)-2-hydroxy-4,5-methylenedioxybenzene (***β*4b** from **1** and **2b**), m.p. 148–150°. ^{1}H-N.m.r. data: δ 2.11 (s, 6 H, 2 Ac), 3.95 (ddd, 1 H, $J_{4,5}$ 8.95, $J_{5,6a}$ 4.38, $J_{5,6b}$ 3.27 Hz, H-5), 4.21 (dd, 1 H, $J_{6a,6b}$ 12.11 Hz, H-6b), 4.30 (dd, 1 H, H-6a), 5.34 (m, 1 H, H-1), 5.47

(dm, 1 H, H-4), 5.86 (dt, 1 H, $J_{2,3}$ 10.21, $J_{1,3} = J_{3,4}$ = 2.50 Hz, H-3), 5.89 (m, 2 H, OCH_2O), 5.94 (dt, 1 H, $J_{1,2} = J_{2,4}$ = 1.60 Hz, H-2), 6.44 (s, 1 H, H-3'), 6.53 (s, 1 H, H-6'), 6.87 (s, 1 H, OH).

Anal. Calc. for $C_{17}H_{18}O_8$: C, 58.28; H, 5.18. Found: C, 58.19; H, 5.14.

1-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-2-hydroxybenzene (**α4c** from **1** and **2c**), isolated as an oil. ^{1}H-N.m.r. data: δ 2.09 (s, 6 H, 2 Ac), 3.94 (dd, 1 H, $J_{4,5} = J_{5,6a} = J_{5,6b}$ 6.60 Hz, H-5), 4.22 (m, 2 H, H-6a,6b), 5.25 (m, 1 H, H-4), 5.49 (m, 1 H, H-1), 6.03 (dt, 1 H, $J_{2,3}$ 10.66, $J_{3,4} = J_{1,3}$ = 2.50 Hz, H-3), 6.27 (ddd, 1 H, $J_{1,2}$ 3.04, $J_{2,4}$ 1.39 Hz, H-2), 6.8–7.3 (m, 4 H, aromatic H), 7.12 (s, 1 H, OH).

Anal. Calc. for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.64; H, 5.88.

1-(4,6-Di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl-2-hydroxybenzene (**β4c** from **1** and **2c**), isolated as an oil. ^{1}H-N.m.r. data: δ 2.10 and 2.12 (2 s, each 3 H, 2 Ac), 3.95 (ddd, 1 H, $J_{4,5}$ 9.21, $J_{5,6a}$ 5.53, $J_{5,6b}$ 3.33 Hz, H-5), 4.21 (m, 2 H, H-6a,6b), 5.31 (m, 1 H, H-1), 5.40 (dm, 1 H, H-4), 5.60 (bs, 1 H, OH), 5.82 (dt, 1 H, $J_{2,3}$ 10.61, $J_{3,4} = J_{1,3}$ = 2.43 Hz, H-3), 5.91 (dt, 1 H, $J_{1,2} = J_{2,4}$ = 1.27 Hz, H-2), 6.7–7.3 (m, 4 H, aromatic H).

Anal. Calc. for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.69; H, 6.07.

1-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-2-hydroxy-5-methoxybenzene (**α4d** from **1** and **2d**), m.p. 68–70°. ^{1}H-N.m.r. data: δ 2.08 (s, 6 H, 2 Ac), 3.78 (s, 3 H, OMe), 3.92 (ddd, 1 H, $J_{4,5}$ 6.56, $J_{5,6a}$ 5.67, $J_{5,6b}$ 3.58 Hz, H-5), 4.21 (m, 2 H, H-6a,6b), 5.25 (m, 1 H, H-4), 5.47 (m, 1 H, H-1), 6.04 (ddd, 1 H, $J_{2,3}$ 10.22, $J_{3,4}$ 2.88, $J_{1,3}$ 1.77 Hz, H-3), 6.27 (ddd, 1 H, $J_{1,2}$ 3.11, $J_{2,4}$ 1.33 Hz, H-2), 6.65 (d, 1 H, $J_{4',6'}$ 3.32 Hz, H-6'), 6.80 (dd, 1 H, $J_{3',4'}$ 8.88 Hz, H-4'), 6.89 (d, 1 H, H-3'), 6.90 (s, 1 H, OH).

Anal. Calc. for $C_{17}H_{20}O_7$: C, 60.71; H, 5.99. Found: C, 60.90; H, 6.06.

1-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-2-hydroxy-4-methoxybenzene (**α4e** from **1** and **2e**), isolated as an oil. ^{1}H-N.m.r. data: δ 2.08 and 2.10 (2 s, each 3 H, 2 Ac), 3.80 (s, 3 H, OMe), 3.92 (ddd, 1 H, $J_{4,5}$ 7.12, $J_{5,6a}$ 5.56, $J_{5,6b}$ 3.33 Hz, H-5), 4.19 (m, 2 H, H-6a,6b), 5.25 (m, 1 H, H-4), 5.41 (m, 1 H, H-1), 6.00 (ddd, 1 H, $J_{2,3}$ 10.44, $J_{3,4}$ 3.01, $J_{1,3}$ 1.51 Hz, H-3), 6.26 (ddd, 1 H, $J_{1,2}$ 3.11, $J_{2,4}$ 1.49 Hz, H-2), 6.3–6.6 (m, 2 H, H-3',5'), 6.94 (d, 1 H, $J_{5',6'}$ 8.20 Hz, H-6'), 7.20 (s, 1 H, OH).

Anal. Calc. for $C_{17}H_{20}O_7$: C, 60.71; H, 5.99. Found: C, 60.59; H, 5.91.

1-(4,6-Di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranosyl)-2-hydroxy-4-methoxybenzene (**β4e** from **1** and **2e**), isolated as an oil. ^{1}H-N.m.r. data: δ 2.06 and 2.09 (2 s, each 3 H, 2 Ac), 3.78 (s, 3 H, OMe), 3.92 (ddd, 1 H, $J_{4,5}$ 9.12, $J_{5,6a}$ 5.11, $J_{5,6b}$ 3.32 Hz, H-5), 4.21 (m, 2 H, H-6a,6b), 5.22 (s, 1 H, OH), 5.38 (dm, 1 H, H-4), 5.55 (m, 1 H, H-1), 5.73 (dt, 1 H, $J_{2,3}$ 10.48, $J_{3,4} = J_{1,3}$ = 2.50 Hz, H-3), 5.88 (dt, 1 H, $J_{1,2} = J_{2,4}$ = 1.81 Hz, H-2), 6.36 (dd, 1 H, $J_{5',6}$, 8.45, $J_{3,5}$, 2.56 Hz, H-5'), 6.38 (d, 1 H, H-3'), 7.15 (d, 1 H, H-6').

Anal. Calc. for $C_{17}H_{20}O_7$: C, 60.71; H, 5.99. Found: C, 60.49; H, 6.03.

3-*tert*-Butyl-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-2-hydroxy-5-methoxybenzene (**α4f** from **1** and **2f**), m.p. 77–79°. ^{1}H-N.m.r. data: δ

1.37 (s, 9 H, ^{t}Bu), 2.00 and 2.02 (2 s, each 3 H, 2 Ac), 2.22 (s, 3 H, Me), 3.89 (ddd, 1 H, $J_{4,5}$ 7.01, $J_{5,6a}$ 6.20, $J_{5,6b}$ 4.09 Hz, H-5), 4.15 (m, 2 H, H-6a,6b), 5.23 (dm, 1 H, H-4), 5.47 (m, 1 H, H-1), 6.00 (ddd, 1 H, $J_{2,3}$ 10.31, $J_{3,4}$ 3.61, $J_{1,3}$ 2.00 Hz, H-3), 6.31 (ddd, 1 H, $J_{1,2}$ 3.03, $J_{2,4}$ 1.33 Hz, H-2), 6.72 (d, 1 H, $J_{4,6}$ 2.66 Hz, H-5'), 7.08 (d, 1 H, H-6'), 7.35 (s, 1 H, OH).

Anal. Calc. for $C_{21}H_{18}O_6$: C, 68.84; H, 4.95. Found: C, 69.04; H, 5.01.

1-(4-*O*-Acetyl-2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranosyl)-2-hydroxy-4,5-methylenedioxybenzene (**α6** from **2b** and **5**) isolated as an oil. ^{1}H-N.m.r. data: δ 1.30 (d, 3 H, $J_{5,6}$ 6.73 Hz, Me-6), 2.09 (s, 3 H, Ac), 4.00 (dq, 1 H, $J_{4,5}$ 4.58 Hz, H-5), 5.01 (m, 1 H, H-4), 5.26 (m, 1 H, H-1), 5.88 (m, 2 H, OCH_2O), 5.98 (ddd, 1 H, $J_{2,3}$ 10.48, $J_{3,4}$ 3.22, $J_{1,3}$ 1.34 Hz, H-3), 6.09 (ddd, 1 H, $J_{1,2}$ 2.69, $J_{2,4}$ 1.01 Hz, H-2), 6.45 (s, 1 H, H-3'), 6.54 (s, 1 H, H-6'), 7.28 (s, 1 H, OH).

Anal. Calc. for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.73; H, 5.47.

1-(4-*O*-Acetyl-2,3,6-trideoxy-β-L-*erythro*-hex-2-enopyranosyl)-2-hydroxy-4,5-methylenedioxybenzene (**β6** from **2b** and **5**), m.p. 132–133°. ^{1}H-N.m.r. data: δ 1.35 (d, 3 H, $J_{5,6}$ 6.45 Hz, Me-6), 2.10 (s, 3 H, Ac), 3.82 (dq, 1 H, $J_{4,5}$ 8.89 Hz, H-5), 5.22 (m, 1 H, H-4), 5.28 (m, 1 H, H-1), 5.81 (dt, 1 H, $J_{2,3}$ 10.31, $J_{3,4} = J_{1,3} =$ 2.60 Hz, H-3), 5.89 (m, 2 H, OCH_2O), 5.91 (dt, 1 H, $J_{1,2} = J_{2,4} = 1.66$ Hz, H-2), 6.43 (s, 1 H, H-3'), 6.52 (s, 1 H, H-6'), 7.33 (s, 1 H, OH).

Anal. Calc. for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.33; H, 5.72.

1-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranosyl)-2-hydroxy-4,5-methylenedioxybenzene (**α8** from **2b** and **7**), isolated as an oil. ^{1}H-N.m.r. data: δ 2.04 and 2.12 (2 s, each 3 H, 2 Ac), 3.95 (ddd, 1 H, $J_{4,5}$ 2.69, $J_{5,6a}$ 7.51, $J_{5,6b}$ 4.84 Hz, H-5), 4.13 (dd, 1 H, $J_{6a,6b}$ 11.57 Hz, H-6a), 4.22 (dd, 1 H, H-6b), 5.10 (dd, 1 H, $J_{3,4}$ 5.11 Hz, H-4), 5.57 (dd, 1 H, $J_{1,2}$ 3.76, $J_{1,3}$ 1.61 Hz, H-1), 5.90 (m, 2 H, OCH_2O), 6.22 (ddd, 1 H, $J_{2,3}$ 10.48 Hz, H-3), 6.42 (dd, 1 H, $J_{2,4}$ <1 Hz, H-2), 6.48 (s, 1 H, H-3'), 6.50 (s, 1 H, H-6'), 7.23 (bs, 1 H, OH).

Anal. Calc. for $C_{17}H_{18}O_8$: C, 58.28; H, 5.18. Found: C, 58.48; H, 5.09.

*Crystallography**. — Crystal data for **β4b**: $C_{17}H_{18}O_8$, M 350.3, colorless prismatic crystals, orthorhombic space group $P2_12_12_1$; cell dimensions, a = 30.259(4) Å, b = 9.641(2) Å, and c = 5.713(1) Å; V = 1666.6(5) Å^3; Z = 4; (CuK_α)λ = 1.54178 Å, μ = 9.1 cm^{-1}; D_c = 1.396 g.cm^{-3}, $F(000)$ = 736. Crystal size 0.33 × 0.08 × 0.49 mm; 1780 reflections measured, 828 with $I > 2\sigma(I)$ used in refinement; $\Delta\rho_{max} = 0.12$, $\Delta\rho_{min} = -0.15$, max 2Θ = 130°. The ω–2Θ scan mode of the Siemens AED single-crystal computer-controlled diffractometer was used for the recording of intensity data. The intensity of a standard reflection was monitored after every 50 measurements and showed good stability of the crystal and the electronics. No correction for absorption was applied because of the size of crystal used.

The structure was solved by direct methods, with MULTAN[22,23], and refined by full-matrix least-squares cycles using the SHELX-76[24] system of computer

*Tables including atom positions, anisotropic thermal parameters, and bond distances and angles have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/412/ *Carbohydr. Res.*, 191 (1989) 241–249.

programs. The final conventional R index was 0.054, R_w = 0.06 (observed reflections only). The hydrogen atoms were located from a Fourier difference synthesis, but not refined.

The scattering factors for all atoms were taken from ref. 25, and both the real and imaginary components of anomalous dispersion were included. Calculations were carried out an a GOULD 6040 Powernode computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma).

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