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SYNTHESIS AND GLYCOSIDATION REACTIONS OF ACETYLATED RACEMIC PSEUDOGLYCALS[1]*

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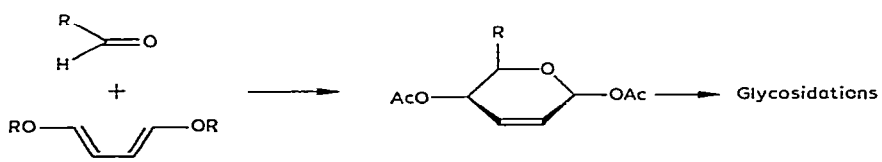
ABSTRACT

The Diels–Alder reaction of 1,3-butadienylene diacetate with activated carbonyl compounds yields *O*-acetylated pseudoglycals (hex-2-enopyranoses). These reactive compounds are used for highly stereoselective syntheses of α-glycosides. Conformational analysis of the pseudoglycals and their derivatives using ^{1}H-n.m.r. data provides new support for the influence of the allylic effect on conformational stability.

INTRODUCTION

Unsaturated carbohydrates[2], especially pseudoglycals[3] (hex-2-enopyranoses), are of value in carbohydrate synthesis, because the double bond may be easily modified by, for instance, hydroxylation[4,5], epoxidation[6], and hydroxyamination[7].

Pseudoglycals may be synthesised conventionally *via* elimination reactions[3,8,9] or by an alkoxylating allyl-rearrangement[10,11]. Achmatowicz and co-workers[12] developed a four-step, *de novo* synthesis of pseudoglycals starting from furfuryl alcohols. However, pseudoglycals should be accessible *via* a Diels–Alder reaction of 1,4-bifunctional 1,3-dienes with a carbonyl compound:



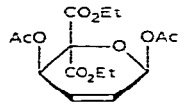
1 R = Ac

We now report on such a synthesis[1]. *trans,trans*-1,3-Butadienylene diacetate (**1**, R = Ac) was selected as the bifunctional diene, because it is readily available[13], the acyl groups are easily cleaved, and 1-*O*-acetylpseudoglycals should be reactive and useful intermediates in glycosidation reactions.

**de novo* Synthesis of Carbohydrates and Related Natural Products, Part 6. For Part 5, see ref. 33.

RESULTS AND DISCUSSION

Diels–Alder reactions. — Under normal pressures, only the more reactive carbonyl compounds act as dienophiles in Diels–Alder reactions[14–16]; under high pressures, experiments with less reactive compounds have been successful[16]. Preliminary investigations showed that **1** did not react with formaldehyde or chloral; however, the more reactive mesoxalic acid and glyoxylic acid esters yielded cycloaddition products[17].



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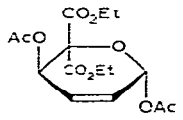

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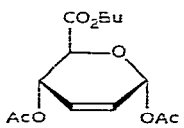
The reaction of **1** with diethyl mesoxalate (140°, 20 h) gave the cyclo-adduct **2** in high yield*. The use of excess of diethyl mesoxalate led to quantitative disappearance of **1**, and therefore no chromatography was necessary in the isolation of **2**, which is thus readily available in large quantities. Under more-drastic conditions (160°, 60 h), **2** was partly isomerised into the α isomer **3****. Acid-catalysed isomerisation of **2** gave the thermodynamically more-stable **3** in quantitative yield.

The reaction of **1** with butyl glyoxylate gave various products, depending on the reaction conditions; the nature of the product mixture was influenced by the purity of the glyoxylate. Alkyl glyoxylates are commonly synthesised by oxidative cleavage of the corresponding dialkyl tartrate with lead tetra-acetate[18]. Complete removal of the contaminant acetic acid resulted in a large loss of product. Therefore, butyl glyoxylate contaminated with ~2% of acetic acid was treated with **1** (125°, 60 h). A mixture of the *α-erythro* compound **4** (38%), the *α-threo* isomer **6** (37%), and the "gulal-uronate" **7** (9%) was obtained in good yield.



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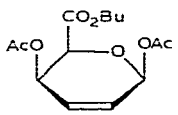

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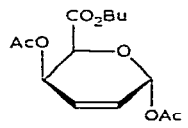

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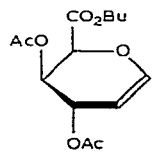

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Because Diels–Alder reactions are usually *cis*-stereospecific, the *exo* and *endo* compounds **4** and **5** were expected to be the first products. However, the presence of acetic acid resulted in quantitative rearrangement of **5** into the more stable α-isomer **6**.

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*Compounds **2–7**, **8a–c**, **9a–c**, **10a–c**, and **11a–c** are racemates; **8d**, **9d**, **10d,e**, and **11e** are mixtures of two diastereomers.

Compounds **2, **3**, and their glycosidation products are classified as C-5-substituted *threo*-hex-2-enopyranosides.

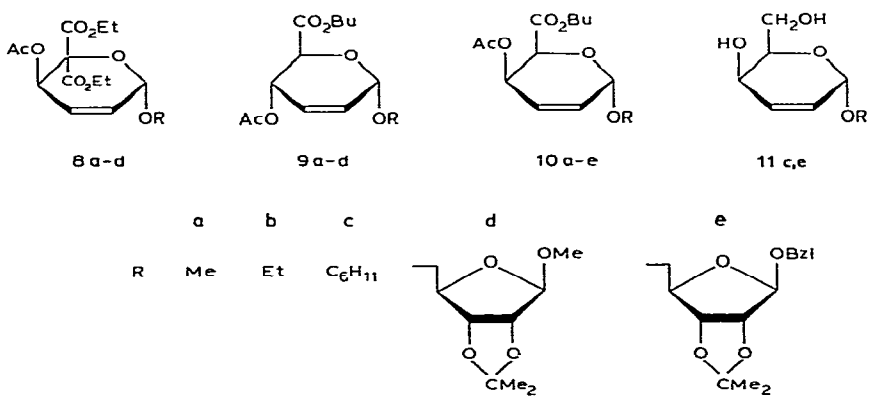
Under milder conditions (110°, 60 h), **1** and pure butyl glyoxylate gave only **4** (13%) and **5** (19%).

The by-product was identified as the butyl "gulal-uronate" **7** by mass- and ^{1}H-n.m.r.-spectroscopy. The mass spectrum of **7**, in contrast to those of **4** and **6**, did not contain a signal (*m/z* 170, corresponding to **1**) indicating retro-Diels–Alder reaction, which is typical for 2,3-unsaturated carbohydrates[19]. The ^{1}H-n.m.r. spectrum of **7** showed a signal for H-1 (δ 6.5, $J_{1,2}$ 6 Hz) typical of acetylated glycals[20]. The configuration of **7** was indicated unequivocally by the ^{1}H-n.m.r. data. Since glucal, allal, galactal, and gulal prefer the $^4H_5$ conformation[20], the small value (1.5 Hz) of $J_{4,5}$ does not accord with the glucal or allal configuration. The value (5.3 Hz) of $J_{2,3}$ is consistent only with a pseudo-equatorial H-3, as in the gulal configuration. All of the other coupling constants are consistent with this configurational assignment[20,21].

The transformation **6** → **7** involves a [3.3]sigmatropic shift. Similar rearrangements of *O*-acetylated, unsaturated carbohydrates are known[22,23], but they require either acid catalysis or higher temperatures and are highly stereoselective. The equilibrium favours the pseudoglycals[24]

Glycosidation reactions. — The acid-catalysed, alkoxylating allyl-rearrangement of acetylated glycals, which is a common and efficient method for the synthesis of pseudoglycals[10], is of growing interest for disaccharide syntheses, because of the highly stereoselective formation of α anomers[25,26]. A mechanism[10,23,24] for this reaction assumes an initial rearrangement glycal → 1-*O*-acetylpseudoglycal. The 1-*O*-acetylpseudoglycals **2–6** allow the reactivity and utility of these compounds in glycoside syntheses[1,17,27] to be investigated.

Thus, **2**, with boron trifluoride as catalyst in acetonitrile, reacted with primary and secondary alcohols quantitatively and with methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside, to give the α-glycosides **8a–d** in good yield. β-Glycosides and other by-products could not be detected. The specific inversion of configuration at C-1 supports the S_N2 mechanism[23]. However, t.l.c. showed that **2** was isomerised, at least partly, into **3** under the conditions of the glycosidation reactions[27]. Under these conditions, **3** reacted as did **2**, to give a similar yield of **8a–d**. This result accords with



the intermediate formation of a resonance-stabilised, allyl-oxo-type cation[1,28-30]; subsequent formation of a nitrilium salt with the acetonitrile solvent also has to be considered[30].

The optimum conditions for the reaction of **2** and **3** were applied to other acetylated pseudoglycals. The *α-erythro* derivative **4** gave the α-glycosides **9a–d** almost quantitatively. According to the ^{1}H-n.m.r. spectra, these compounds were contaminated with <5% of β-glycoside. From the α- (**6**) and *β-threo* derivative (**5**), only the *α-threo*-glycosides **10a–e** were obtained in good yields. β-Glycosides or other by-products were not observed in the *threo* series. Therefore, α-glycosides and α-disaccharides are accessible by a simple, two-step process from glyoxylate and 1,3-butadienylene diacetate[31].

Reduction of **10c** and **10e** with lithium aluminium hydride gave the *α-threo*-hex-2-enopyranosides **11c** and **11e**, respectively, in good yields. Similar reduction

TABLE I

^{1}H-N.M.R. DATA[a]

	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*OAc*	*OCH$_3$*	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
2	6.48	5.94	6.28	5.90	—	2.04 2.12		1.5	1	11	6	—
3	6.57	5.89	6.37	5.75	—	2.04 (6 H)		3	1.5	10	5.5	—
4	6.37	5.88	5.98	5.54	4.38	2.06 (6 H)		1.5	[b]	[b]	2	9.5
5	6.35	5.95	6.26	5.37	4.52	2.02 2.12		1	1	10	5.5	3
6	6.47	6.06	6.28	5.33	4.73	2.00 2.04		3	0	10	5.5	3
7	6.60	5.01	4.88	5.26	4.47	2.02 2.06		5.6	$J_{2,4}$ 2	5.3	1.3	1.5
8a	5.10	5.91	6.20	5.72	—	2.00	3.47	3	1.5	10	5.5	—
8b	5.26	5.93	6.22	5.73	—	2.02		2.75	1	10	5.5	—
8c	5.40	5.85	6.20	5.71	—	2.00		2.75	1.5	10	5.5	—
8d	5.27	5.97	6.26	5.75	—	2.00		2.75	1.25	10	5.5	—
9a	5.02	5.85–6.10		5.56	4.40	2.08	3.48	[b]	[b]	[b]	1.5	9
9b	5.16	5.90–6.10		5.55	4.42	2.07		[b]	[b]	[b]	1.5	9
9c	5.25	5.85–6.10		5.55	4.46	2.07		[b]	[b]	[b]	[b]	9
9d	5.14	5.85–6.05		5.54	[b]	2.07		[b]	[b]	[b]	[b]	9
10a	5.07	5.99	6.14	5.27	4.72	2.00	3.47	2.5	0	10	5	3
10b	5.19	6.00	6.15	5.28	4.76	2.02		2.5	0	10	4.5	3
10c	5.31	5.96	6.12	5.27	4.78	2.00		2.5	0	10	5	3
10d	5.19	6.00	6.15	5.27	4.76	2.00		2.5	0	10	5	3
10e	5.19	5.96	6.15	5.27	4.76	2.02		2.5	0	10	4.5	3
11c[c]	5.06	5.73	5.98	[b]	[b]	4.55 (OH)		3	0	10	5	[b]
11e[c]	4.96	5.75	6.02	[b]	[b]			3	0	10	5	[b]

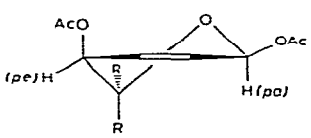
[a]80 MHZ, $CDCl_3$ (internal Me_4Si), δ scale. [b]Not determined. [c]In $(CD_3)_2SO$.

of the *erythro* derivative **9c** was less successful. By-products from eliminations and reductive rearrangement to 3-deoxyglycals were formed[27], a phenomenon observed[32] with α-*erythro*-pseudoglycals.

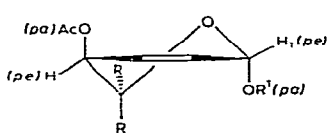
With methanol or ethanol and boron trifluoride-catalysis, **7** gave the known α-*threo*-glycosides **10a** and **10b**, respectively, as the sole reaction products, reflecting neighbouring-group participation[11,23], because the C-3 epimer, galactal, did not react under these conditions[4]. The formation of identical glycosides from **6** and **7** indicates that a preliminary separation of these compounds is not necessary. Glycosidations were therefore carried out with the mixture of **4**, **6**, and **7**, leading[27,33] to an easily separable mixture of **9** and **10**.

Conformational analysis. — 2,3-Unsaturated pyranosides prefer[25,34,35] the half-chair (*H*) conformation. Conformational analysis of pseudoglycals requires an evaluation of steric effects (mainly 1,3-diaxial interactions), the anomeric effect, and the allylic effect. The last effect favours a pseudoaxial (*pa*) position for electron-withdrawing substituents (X) at C-4 (and C-1), because of stabilising interactions between the π-orbitals of the double bond and the empty σ*-orbital of the C–X bond. However, the allylic effect[36] has been considered only occasionally until recently[7,25,27,37].

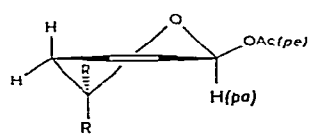
A strong influence of the allylic effect on conformational equilibria is shown by the 5-*C*-ethoxycarbonyl-*threo*-hex-2-enopyranosides **2**, **3**, and **8a–d**. The β-derivative **2** prefers the $^{\circ}H_5$ conformation, according to ^{1}H-n.m.r. data (see Table 1). The coupling constants $J_{1,2}$ 1.5 and $J_{3,4}$ 6.0 Hz indicate H-1 to be *pa* and H-4 to be *pe*. This requires *cis*-1,4-diacetoxy groups and an $^{\circ}H_5$ conformation; the $^5H_0$ conformation would involve an unfavourable 1,3-diaxal interaction. Clearly, the anomeric and allylic effects of the anomeric center do not compensate for the unfavourable 1,3-diaxial interaction and the favourable allylic effect of AcO-4.



2 ($^{\circ}H_5$)



3, 8a-d ($^{\circ}H_5$)



12 ($^{\circ}H_5$)

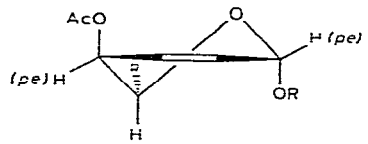
R = CO_2Et

The α anomers **3** and **8a–d** also prefer $^{\circ}H_5$ conformations. Both allylic substituents are *pa* ($J_{1,2}$ 2.75–3.0, $J_{3,4}$ 5.5 Hz; see Table 1), which affords the greatest electronic stabilisation. Thus, the allylic effect associated with AcO-4 compensates for the unfavourable 1,3-diaxial interaction involving AcO-1 and EtOOC-5*a*. The importance of this allylic effect is indicated by the fact that the analogous 4-deoxy compound[22] **12** adopts an $^{\circ}H_5$ conformation with AcO-1 *pe*.

Complete analysis of the ^{1}H-n.m.r. data for the α-*erythro*-pseudoglycals **4** and **9a–d** was not possible, because the signals for H–1 appeared as broad, unresolved

singlets, and those for H–2 and H–3 had almost identical chemical shifts and couplings which could not be assigned; decoupling experiments were not successful. However, the chemical shifts for H–4 and H–5 and the $J_{4,5}$ coupling of 9 Hz (see Table I) were established. These data indicate the *erythro* structure and prove the α configuration, because *β-erythro*-pseudoglycals prefer the ^5H_o(D) conformation and have[7,38] $J_{4,5}$ 2.2 Hz. This conformational change of *β-erythro* derivatives confirms that two allylic effects and one anomeric effect outweigh unfavourable 1,3-diaxial interactions.

The ^{1}H-n.m.r. spectra of the *α-threo*-glycosides **6**, **10a–e**, and **11c,e** were easily assigned (see Table I). The coupling constants $J_{1,2}$ 2.5–3.0 and $J_{3,4}$ 4.5–5.5 Hz indicate preferential *pe* positions for H–1 and H–4, which corresponds to an $^oH_5$(D) conformation. The *β-threo*-glycoside **5**, with $J_{3,4}$ 5.5 Hz, also adopts an $^oH_5$(D) conformation, and the $J_{1,2}$ value (1.0 Hz) establishes a *pa* position for H–1 and the *β* configuration.



6, 10a-e [$^oH_5$ (D)]

Thermodynamically, the *α-threo*-hex-2-enopyranosides are the most stable isomers of the four possible diastereomers, if the allylic effects are also considered. This explains the more stereoselective, alkoxylating allyl-rearrangement of tri-*O*-acetylgalactal into *α-threo*-glycosides[11] than observed in the corresponding rearrangement of tri-*O*-acetyl-D-glucal into the *α-erythro* derivatives[10]. It also accounts for the clean glycosidation reactions of **6** and for the quantitative isomerisation **5** → **6**, whereas the *α-erythro* isomer **4** gives minor amounts of by-products.

EXPERIMENTAL

General. — Melting points are uncorrected. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Bruker CW-80 spectrometer. *trans, trans*-1,3-Butadienylene diacetate (**1**) was prepared from cyclo-octatetraene[13]. R_F values refer to t.l.c. performed on silica gel (Merck) with the solvent systems noted.

*Ethyl 1,4-di-O-acetyl-2,3-dideoxy-5-C-ethoxycarbonyl-β-*DL-threo-*hex-2-enopyranuronate* (**2**). — A solution of **1** (34 g, 0.2 mol), dimethyl mesoxalate (52 g, 0.3 mol), and hydroquinone (30 mg) in benzene (80 ml) was kept at 140° for 20 h in an autoclave and then concentrated. The residue was eluted from silica gel with ethyl acetate–light petroleum (b.p. 40–60°) (3:7), to separate polymeric material and excess of diethyl mesoxalate, and give **2** (62 g, 87%) as a slightly yellow oil.

Anal. Calc. for $C_{15}H_{20}O_9$: C, 52.33; H, 5.85. Found: C, 52.40; H, 5.81.

See Table I, for ^{1}H-n.m.r. data.

*Ethyl 1,4-di-O-acetyl-2,3-dideoxy-5-C-ethoxycarboyl-α-*DL-threo-*hex-2-enopyranuronate* (**3**). — A solution of **2** (1.0 g, 3 mmol) in acetic anhydride–acetic acid (15 ml, 1:1) and toluene-*p*-sulfonic acid (0.25 g) was stirred at room temperature for 24 h. Chloroform (150 ml) was added, the mixture was washed with saturated, aqueous sodium hydrogencarbonate (3 × 50 ml), dried (Na_2SO_4), and concentrated, to yield **3** (920 mg, 92%) as a colourless oil which crystallised on storage: m.p. 94° (from cyclohexane).

Anal. Calc. for $C_{15}H_{20}O_9$: C, 52.33; H, 5.85. Found: C, 52.40; H, 5.85.

See Table I, for ^{1}H-n.m.r. data.

*Butyl 1,4-di-O-acetyl-2,3-dideoxy-α-*DL-erythro- (**4**) and -threo-*hex-2-enopyranuronate* (**6**), *and butyl 3,4-di-O-acetyl-2,6-anhydro-5-deoxy-*DL-xylo-*hex-5-enonate* (*butyl "gulal-uronate"*) (**7**). — A solution of **1** (9 g, 53 mmol), butyl glyoxylate (9 g, 69 mmol: containing 2% of acetic acid), and hydroquinone (20 mg) in anhydrous benzene (10 ml) was kept at 125° for 60 h and then concentrated, and the residue was eluted from silica gel with benzene–acetone (9:1), to give, first, **7** (1.4 g, 9%) as a slightly yellow oil, R_F 0.52.

Anal. Calc. for $C_{14}H_{20}O_7$: C, 56.01; H, 6.71. Found: C, 56.15; H, 6.71.

Eluted second was **4** (6.1 g, 38%), as a slightly yellow oil, R_F 0.48.

Anal. Found: C, 56.27; H, 6.79.

Eluted third was **6** (5.9 g, 37%), as a slightly yellow oil, R_F 0.33.

Anal. Found: C, 56.17; H, 6.89.

See Table I, for ^{1}H-n.m.r. data.

*Butyl 1,4-di-O-acetyl-2,3-dideoxy-β-*DL-threo-*hex-2-enopyranuronate* (**5**). — By the method described above, **1** (4.3 g, 2 mmol) was treated with butyl glyoxylate (2.8 g, 2.1 mmol, free of acetic acid), to give **4** (0.77 g, 13%), and **5** (1.16 g, 19%) as a slightly yellow oil, R_F 0.31.

See Table I, for ^{1}H-n.m.r. data.

Conversion of **2–7** *into glycosides.* — (*a*) A solution of 1-*O*-acetylpseudoglycal **2–6** (2 mmol) and anhydrous alcohol (1.5 g of methanol, ethanol, or cyclohexanol) in anhydrous acetonitrile (50 ml) was treated with boron trifluoride etherate (0.5 ml) at 5° for 3 h. The mixture was neutralised with saturated, aqueous sodium hydrogencarbonate (40 ml) and extracted with chloroform (3 × 50 ml), and the combined extracts were dried (Na_2SO_4) and concentrated to dryness, to give analytically pure products **8a–c**, **9a–c**, and **10a–c** either as colourless or slightly yellow oils.

See Table II for yields and analyses, and Table I for ^{1}H-n.m.r. data.

(*b*) Using the method described in (*a*), **2–7** (2 mmol) and methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (2.2 mmol) were allowed to react. The colourless oils obtained were eluted from silica gel with ethyl acetate; R_F values: **8d** 0.54, **9d** 0.58, **10d** 0.43, and **10e** 0.71.

See Table II for yields and analyses, and Table I for ^{1}H-n.m.r. data.

*Cyclohexyl 2,3-dideoxy-α-*DL-threo-*hex-2-enopyranoside* (**11c**). — A solution of **10c** (2.2 g, 6.45 mmol) in anhydrous ether (10 ml) was added to a suspension of lithium aluminum hydride (0.5 g) in ether (6 ml) at room temperature. After 4 h,

TABLE II

YIELDS AND ANALYSES OF COMPOUNDS **8–10**

Compound	*Starting material*	*Yield (%)*	*Analysis*				
			Formula	*Calc.*		*Found*	
				C	*H*	*C*	*H*
8a	2	98	$C_{14}H_{20}O_8$	53.16	6.37	53.13	6.43
	3	95					
8b	2	98	$C_{15}H_{22}O_8$	54.54	6.71	54.33	6.66
	3	98					
8c	2	96	$C_{19}H_{28}O_9$	59.36	7.34	59.15	7.33
	3	97					
8d	2	51	$C_{22}H_{32}O_{12}$	54.10	6.60	54.00	6.55
	3	48					
9a	4	94	$C_{13}H_{20}O_6$	57.34	7.40	56.93	7.24
9b	4	91	$C_{14}H_{22}O_6$	58.73	7.74	58.73	7.71
9c	4	93	$C_{18}H_{28}O_6$	63.51	8.29	63.68	8.37
9d	4	50	$C_{21}H_{32}O_{10}$	56.75	7.26	56.64	7.32
	5	94					
10a	6	98	$C_{13}H_{20}O_6$	57.34	7.40	57.16	7.58
	7	94					
10b	6	96	$C_{14}H_{22}O_6$	58.73	7.74	58.62	7.72
	7	91					
10c	5	98	$C_{18}H_{28}O_6$	63.51	8.29	63.32	8.28
	6	98					
10d	6	52	$C_{21}H_{32}O_{10}$	56.75	7.26	56.69	7.27
10e	6	50	$C_{27}H_{36}O_{10}$	62.30	6.97	62.08	7.03

water (10 ml) was slowly added at 0° and the mixture was stirred for 20 min. The slurry of aluminum hydroxide was dissolved by adding dilute sulfuric acid, and excess of acid was neutralised with solid sodium hydrogencarbonate. After addition of water (10 ml), the mixture was extracted with ether (6 × 30 ml), and the combined extracts were treated with saturated, aqueous sodium chloride, dried (Na_2SO_4), and concentrated. The residue was eluted from silica gel with ethyl acetate, to give **11c** (970 mg, 66%), m.p. 98° (from cyclohexane), R_F 0.36.

Anal. Calc. for $C_{12}H_{20}O_4$: C, 63.15: H, 8.83. Found: C, 62.92; H, 8.80.

See Table I for ^{1}H-n.m.r. data.

*Benzyl 5-O-(2,3-dideoxy-α-*DL*-threo-hex-2-enopyranosyl)-2,3-O-isopropylidene-β-*D*-ribofuranoside* (**11e**). — Using the method described above, **10e** (3.35 g, 6.45 mmol) and benzyl 2,3-*O*-isopropylidene-β-D-ribofuranoside were converted into **11e** (2.0 g, 76%), which was obtained as a colourless oil after elution from silica gel with ethyl acetate and had R_F 0.48.

Anal. Calc. for $C_{21}H_{28}O_8$: C, 61.75: H, 6.91. Found: C, 61.85; H, 6.80.

See Table I for ^{1}H-n.m.r. data.

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