

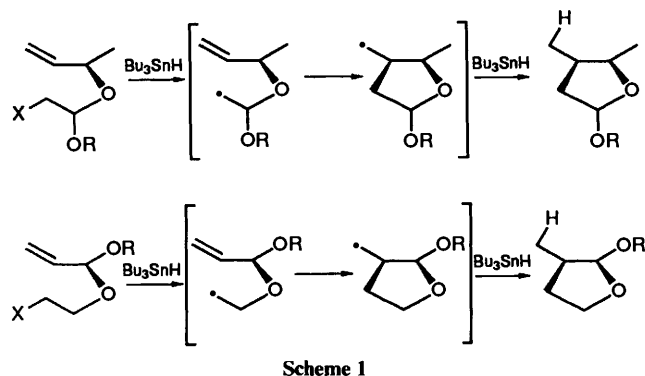
Radical Cyclization of Some Unsaturated Carbohydrate-Derived Acetals†¹

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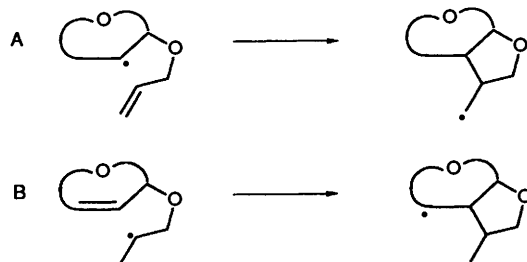
Treatment of halogeno acetals derived from deoxy-D-hexenopyranosides of *erythro* and *threo* configuration with tributyltin hydride with a radical initiator gave fused pyranofuranosides. This allowed the completely stereo and regio-specific introduction of a functionalized carbon chain at the C-2 or C-3 position of some carbohydrate templates.

The use of free-radical reactions in carbon-carbon bond formation is now widely recognized and has been recently reviewed.² Free-radical reactions are of special interest because they allow carbocyclization or regio- and stereo-specific introduction of carbon chains on a suitable template. Owing to the mildness of the reaction conditions, free-radical reactions can be conducted either without or with sensitive protecting groups. This has prompted numerous studies of free-radical reactions in the carbohydrate field; in particular, free-radical formation of carbon-carbon bonds has been extensively studied.³⁻⁵ The pioneering works of Stork⁶ and Ueno⁷ using allylic alcohols and 'a detachable radical' to promote the favoured 5-*exo* cyclization giving a five-membered ring which can be opened on further elaboration, has stimulated a considerable body of work and has led to some achievements in the synthesis of natural products.⁸ This 'acetal' methodology can be used in two different ways to introduce a functionalized carbon chain at the α position of the directing allylic alcohol with predicted stereochemistry, as depicted in Scheme 1. In connection with a general programme of exploration of new methods for synthesis of C-branched-chain sugars,⁹ we tried to apply this methodology to unsaturated carbohydrates. Two main approaches can be considered, depending on the role of the sugar template as the radical donor (Scheme 2, A) or the radical acceptor (Scheme 2, B). We have chosen to explore this latter approach and reported some time ago our preliminary results along these lines,¹⁰ almost simultaneously with other groups,¹¹ the other approach also being investigated at the same time.¹² We have now extended our previous studies to other substrates and we report here the full details of this study.



Scheme 1

Allylic alcohols are readily available carbohydrate substrates *via* the Ferrier reaction of glycols with alcohols in the presence of boron trifluoride.¹³ Obviously our study began with the allylic derivative **1** prepared from diacetate **15**. Standard

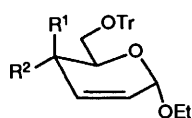


Scheme 2

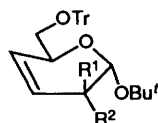
iodoacetalation of this alcohol **1** led to the corresponding ketal **2** as a 1:1 mixture of epimers at the newly formed chiral centre. Treatment of the ketal **2** with tributyltin hydride in the presence of the radical initiator azoisobutyronitrile (AIBN) in refluxing benzene at 0.02 mol dm⁻³ concentration led to the expected cyclized compound **11** as a 1:1 separable mixture of anomers at the furan acetal centre. Similarly, the ketal **7** was prepared from the 2-hydroxy glucal according to standard procedures, and treated as above to give the furanoside **13**. The structure of compounds **11** and **13** was established on the basis of ¹H NMR spectroscopy which showed a large coupling constant of 7-8.5 Hz for the protons at the expected *cis* ring junction. These results demonstrated the ability of 2,3- and 3,4-unsaturated sugars to behave as radical acceptors, allowing the axial introduction of the carbon chain at C-3. In order to check the possibility of introducing the same chain at C-3, but in an equatorial orientation, we prepared the unsaturated ketals **5** and **10**, epimers at C-4 and C-2 of compounds **2** and **7**, respectively. Owing to some difficulties encountered in the Ferrier rearrangement of tri-*O*-acetyl-D-galactal, the synthesis was planned to start from compounds **1** and **6** which were converted into the corresponding epimeric benzoates **3** and **8** under Mitsunobu conditions.¹⁴ Further debenzoylation and iodoacetalation gave the expected ketals **5** and **10**. Radical cyclization of these ketals proceeded in good yield to give the separable furanopyranosides **12** and **14**.

Radical cyclization of iodo bisacetals was next examined. Halogenoacetalation of the allylic hemiacetal **16** gave an inseparable mixture of four isomers **17** owing to the formation of two anomeric centres. The α : β ratio was 3:1 whatever the experimental conditions used. When treated with tributyltin hydride under the above conditions, two sets of products were isolated (83%) and separated. Compound **30** was obtained as a 1:1 mixture of epimers at furan acetal centre whereas its diastereoisomer **35** was obtained as a pure *exo*-(*S*)-isomer on the basis of its ¹H NMR spectrum. The fact that no *endo* isomer was detected in the cyclization products could be explained in terms of an electrostatic repulsion, in the transition state, between the ring oxygen and the oxygen of the ethoxy group of the (*R*) iodoketal **17**. However, under these conditions, direct

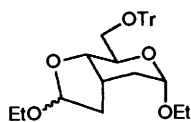
† Contribution from the Laboratoire de Procédés Moléculaires, Université de Nancy I, Institut National Polytechnique de Lorraine.



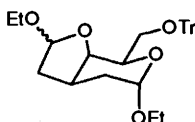
- 1 $R^1 = H, R^2 = OH$
 2 $R^1 = H, R^2 = OCH(OEt)CH_2I$
 3 $R^1 = OBz, R^2 = H$
 4 $R^1 = OH, R^2 = H$
 5 $R^1 = OCH(OEt)CH_2I, R^2 = H$



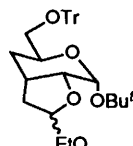
- 6 $R^1 = H, R^2 = OH$
 7 $R^1 = H, R^2 = OCH(OEt)CH_2I$
 8 $R^1 = OBz, R^2 = H$
 9 $R^1 = OH, R^2 = H$
 10 $R^1 = OCH(OEt)CH_2I, R^2 = H$



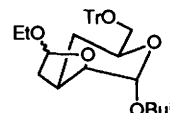
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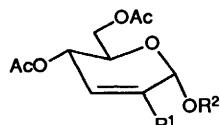
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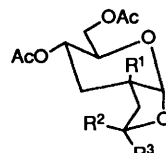
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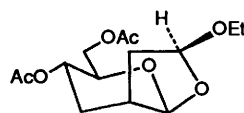
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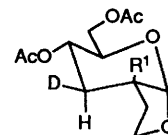
- 15 $R^1 = H, R^2 = Et$
 16 $R^1 = H, R^2 = H$
 17 $R^1 = H, R^2 = CH(OEt)CH_2I$
 18 $R^1 = H, R^2 = CH(OEt)CH_2Br$
 19 $R^1 = H, R^2 = CH(OEt)Me$
 20 $R^1 = H, R^2 = CH_2CH_2I$
 21 $R^1 = H, R^2 = CH_2CH_2Br$
 22 $R^1 = H, R^2 = CH_2CH_2D$
 23 $R^1 = H, R^2 = CH_2CH_2CH_2Br$
 24 $R^1 = H, R^2 = Pr$
 25 $R^1 = H, R^2 = COCH_2Br$
 26 $R^1 = H, R^2 = Ac$
 27 $R^1 = OAc, R^2 = CH_2CH_2Br$
 28 $R^1 = OAc, R^2 = Et$
 29 $R^1 = OAc, R^2 = CH_2CH_2D$

Tr = CPh₃

- 30 $R^1 = H, R^2, R^3 = H, OEt$
 31 $R^1 = H, R^2, R^3 = H, OH$
 32 $R^1 = H, R^2, R^3 = O$
 33 $R^1 = R^2 = R^3 = H$
 34 $R^1 = OAc, R^2 = R^3 = H$



35

36 R = H
37 R = OAc**Table 1** Cyclization of α -halogeno acetals

Entry	Starting compound	Method	Time (h)	Products (yield %)
1	2	C	1	11a (42), 11b (43)
2	2	D	1	11a (40), 11b (42)
3	5	D	1	12a (50), 12b (46)
4	7	C	0.5	13a (45), 13b (44)
5	10	D	3	14a (42), 14b (40)
6	17	C	0.75	30 (50), 35 (6), 19 (31)
7	17	D	1.5	30 (67), 35 (16), 19 (16)
8	18	D	0.25	30 (68), 35 (25), 19 (5)

reduction of iodine occurred to give the acetal **19** in ~31% yield. By using the 'catalytic method' introduced by Stork¹⁵ ($Bu_3SnCl, NaBH_3CN$) the extent of reduction was decreased to 16%. Similar results were obtained in the cyclization of the bromo acetals **18** and in this case the reduced acetal was isolated in only 5% yield. The structure of the cyclized compounds was again established on the basis of ¹H NMR data, but in this case the anomeric mixture of products **30** was in turn transformed into the single lactone **32**. Acid hydrolysis of the bisacetal **30** gave the corresponding hemiacetal **31**, which retained the bicyclic structure and was subsequently oxidized to the lactone

32, the structure of which was more conveniently ascertained. At this point it is interesting to note that the lactone **32** could be obtained more directly through cyclization of α -acyl radicals generated from the corresponding α -bromo acetate. Although such cyclization using activated and unactivated olefins have been reported,¹⁶ all attempts to cyclize the bromo ester **25** gave only the corresponding acetate **26**. This could be attributed to the lower reactivity of bromo esters with regards to iodo esters as recently pointed out by Hanessian.¹⁷ On the other hand, we examined the free radical cyclization of the halogeno acetals **17** by using the halogen-transfer method developed by Curran ($Bu_3Sn-SnBu_3, hv$),¹⁸ which would have the advantage of introducing an iodine atom at the C-3 position; however, all attempts were unsuccessful.* The results of these cyclizations are summarized in Table 1.

Halogeno acetals **17** or **18** being complex mixtures of anomers, it seemed to be desirable to find a radical-donor chain more conveniently anchored at C-1. Therefore several unsaturated α -glycosides were prepared from readily available tri-*O*-acetyl-D-glucal and tri-*O*-acetyl-2-hydroxy-D-glucal. By using

* Such a functionalization has been described by Nougier *et al.* in a work related to ours, using the photochemically induced free-radical addition of sulfonyl halides to 1,6-dienes: see ref. 11f.

Table 2 Cyclization of β -halogeno ethers and other compounds

Entry	Starting compound	Method	Time (h)	Products (yield %)
1	20	D	0.5	33 (93), 15 (6)
2	21	C	6	33 (76), 15 (22)
3	21	D	6	33 (88), 15 (8)
4	21	E	3.5	33 (95), 15 (4)
5	23	C	3.5	24 (99)
6	23	D	6	24 (99)
7	26	D	8	34 (57), 28 (24)
8	21	C	2	36 (84), 22 (6)
9	26	C	4	37 (62), 29 (32)

Method C: Bu_3SnH (1.1 mol equiv.), AIBN (cat.) 0.02 mol dm^{-3} in degassed benzene, reflux. Method D: NaBH_3CN (2 mol equiv.), AIBN (cat.), Bu_3SnCl (0.1 mol equiv.) in degassed *tert*-butyl alcohol. Method E: Bu_3SnH (1.1 mol equiv.) in degassed benzene added slowly with a motor-driven syringe, AIBN (cat.) 0.02 mol dm^{-3} in degassed benzene, reflux.

well known chemistry, the halogeno glycosides **20**, **21**, **23** and **27** were prepared (as $\alpha:\beta \approx 9:1$ mixtures) and tested in the cyclization reaction. For the 2-halogenoethyl glycosides **20**, **21** and **27** the cyclization gave good yields of the furanopyranosides **33** and **34** respectively, together with a small amount of the reduced derivative, whereas the 3-bromopropyl glycoside **23** gave only the corresponding propyl glycoside **24**, thus confirming that 5-*exo* cyclization is a strongly favoured process with regard to the 6-*exo* one.

It appeared, from the above results, summarized in Table 2, that the intermediate radicals generated from the glycosidic side chain were more easily trapped by tributyltin hydride than are those radicals generated on the side chains anchored at C-2 or C-4. This reduction could arise from a 1,5-hydride shift¹⁹ from the anomeric centre to the intermediate radical, thus allowing the formation of an anomeric radical which will subsequently react with tin hydride. If it was the case, the radical cyclization of 2-bromoethyl glycosides **21** and **27** with tributyltin deuteride would afford the reduced glycoside labelled at the anomeric centre. For both cyclizations, small amounts of the glycosides **22** and **29** were isolated and found to be labelled on the methyl group, thereby demonstrating that reduction arose from a bimolecular process. Interestingly, in the corresponding cyclized compounds **36** and **37**, the deuterium atom was specifically introduced at the C-3 position in a *trans* orientation with the C-2 substituent. The trapping of such intermediate radicals with activated olefins in a *trans* fashion has been reported by Ferrier.¹¹

This study has demonstrated that unsaturated sugars were good acceptors in the radical cyclization of α -halogeno acetals with tributyltin hydride. This allows a direct synthesis of C-2 and C-3 branched-chain sugars with a predictable orientation and complete regio- and stereo-control. Reactions were generally conducted using standard conditions and in the presence of acid- or base-sensitive protecting groups. Reduction has been observed only when the radical carrying the chain was anchored at the anomeric centre. This could be attributed to a slower cyclization rate at C-2 compared with that at C-3. This was also true for the cyclization of vinylic radicals, as demonstrated in the following paper.

Experimental

¹H NMR spectra were recorded with a Bruker Aspect 3000 spectrometer operating at 400 MHz, using deuteriochloroform as solvent. Assignments were confirmed by double irradiation. Chemical shifts are reported relative to internal SiMe_4 , and *J*-values are given in Hz. TLC was performed on silica gel (Merck

60 F₂₅₄). Column chromatography used silica gel (Merck 60 70–23 mesh). Mixtures of ethyl acetate (A) or diethyl ether (E) and hexane (H) were used as eluents. Optical rotations were measured on a Perkin-Elmer 141 polarimeter at 20 °C; units for $[\alpha]$ are 10⁻¹ deg $\text{cm}^2 \text{g}^{-1}$. M.p.s were measured in capillary tubes and are uncorrected. The elementary analyses were performed by the *Service Central de Microanalyses du CNRS* at Vernaison, France. Elementary analyses of iodo ketals were not performed owing to their instability.

General Procedure A: Halogenoacetalation.—To a solution of the alcohol (1 mmol) in methylene dichloride (5 cm^3), stirred at –20 °C in the dark under nitrogen, was added a mixture of *N*-iodo- or *N*-bromo-succinimide (NIS or NBS) (1.55 mmol) and ethyl vinyl ether (1.8 mmol) in methylene dichloride (1 cm^3). The reaction mixture was stirred until TLC indicated complete reaction and was then diluted with methylene dichloride, washed successively with aq. sodium thiosulfate and water, dried (MgSO_4), and concentrated under reduced pressure. Chromatography of the resultant residue on silica gel gave the 1:1 diastereoisomeric mixture of the α -halogeno acetal.

General Procedure B: Halogenoacetalation.—To a solution of the alcohol (1 mmol) in methylene dichloride (5 cm^3) stirred in the dark at room temperature under nitrogen was added, in four separate portions during 2 h, a mixture of NIS or NBS (1.55 mmol) and ethyl vinyl ether (1.8 mmol) in methylene dichloride (1 cm^3). The reaction mixture was stirred until TLC indicated complete reaction and was then treated according to the general procedure A.

General Procedure C: Cyclization.—To a solution of the iodo or bromo compound (1 mmol) and AIBN (16 mg, 0.1 mmol) in refluxing, degassed benzene (50 cm^3) under nitrogen was added tributyltin hydride (0.3 cm^3 , 1.1 mmol) and the mixture was stirred until TLC indicated complete reaction. The solvent was removed, and the products were separated by column chromatography on silica gel.

General Procedure D: Cyclization (Catalytic Method).—To a solution of bromo or iodo compound (1 mmol) in degassed *tert*-butyl alcohol (5 cm^3), were added AIBN (16 mg, 0.1 mmol), sodium cyanoborohydride (126 mg, 2 mmol) and tributyltin chloride (0.027 cm^3 , 0.1 mmol). The mixture was refluxed under nitrogen until TLC indicated complete reaction, then 3% aq. NH_4OH (1 cm^3) was added and the solvent was removed. The product was extracted with methylene dichloride, washed successively with brine and water, dried (MgSO_4) and concentrated under reduced pressure to give the crude products, which were separated by column chromatography on silica gel.

General Procedure E: Cyclization (Slow Addition).—The bromo or iodo compound (1 mmol) was dissolved in degassed benzene (50 cm^3) with AIBN (16 mg, 0.1 mmol) and refluxed under argon. A solution of tributyltin hydride (0.3 cm^3 , 1.1 mmol) in benzene (5 cm^3) was slowly added with a motor-driven syringe over a period of 4 h. The mixture was stirred under these conditions until TLC indicated complete reaction. After removal of the solvent, the products were separated by column chromatography on silica gel.

General Procedure F: Glycosylation.¹³—To a stirred solution of the tri-*O*-acetyl-D-glucal or 2-acetoxy-D-glucal (1 mmol) in methylene dichloride (5 cm^3) at room temperature were added successively the alcohol (1.1 mmol) and boron trifluoride diethyl ether (0.03 cm^3 , 0.1 mmol). The mixture was stirred until TLC control indicated complete reaction. Pyridine (0.1 cm^3) was then added and the reaction mixture was extracted with

methylene dichloride ($3 \times 50 \text{ cm}^3$), and the combined extracts were washed with water, dried (MgSO_4) and concentrated under reduced pressure. Purification by chromatography gave the unsaturated glycoside.

Ethyl 2,3-Dideoxy-4-O-(1'-ethoxy-2'-iodoethyl)-6-O-trityl- α -D-erythro-hex-2-enopyranoside 2.—Obtained from compound **1**²⁰ as a diastereoisomeric mixture (1'S:1'R, 1:1) according to general procedure A (1 mmol, 2.5 h; 460 mg, 75%) or general procedure B (1.4 mmol, 3 h; 687 mg, 80%); R_f 0.5 (H:A 6:1); ν/cm^{-1} 1600 (C=C); δ_{H} 1.0 (1.5 H, t, OCH_2Me), 1.17 (1.5 H, t, OCH_2Me), 1.26 (1.5 H, t, OCH_2Me), 1.30 (1.5 H, t, OCH_2Me), 2.82 (1 H, $J_{1,2} = J_{1',2'} = 5.5$, 2'-H^A, 2''-H^A), 2.94 (0.5 H, dd, $J_{1',2'}$ 4.5, J_{gem} 10.5, 2'-H^B), 3.30–3.66 (5.5 H, m, 2 OCH_2Me , 5-H^B, 2''-H^B), 3.90–4.06 (2 H, m, $J_{5,6}$ 2.5, $J_{5,6'}$ 5.5, J_{gem} 9.5, 6-H₂), 4.19 (0.5 H, ddd, $J_{1,4}$ 1, $J_{3,4}$ 2, $J_{4,5}$ 9.5, 4-H^A), 4.28 (0.5 H, ddd, $J_{1,4}$ 1, $J_{3,4}$ 2, $J_{4,5}$ 9.5, 4-H^B), 4.43 (0.5 H, t, 1'-H^A), 4.56 (0.5 H, dd, $J_{1',2'}$ 6.5, 1'-H^B), 5.09 (0.5 H, ddd, $J_{1,2}$ 1, $J_{1,3}$ 2, 1-H^A), 5.11 (0.5 H, ddd, $J_{1,2}$ 1, $J_{1,3}$ 2, 1-H^B), 5.79 (0.5 H, ddd, $J_{2,3}$ 10, 3-H^A), 5.82 (0.5 H, ddd, $J_{2,3}$ 10, 3-H^B), 5.99 (0.5 H, dd, 2-H^A), 6.03 (0.5 H, dd, 2-H^B) and 7.15–7.60 (15 H, m, Ph).

Ethyl 4-O-Benzoyl-2,3-dideoxy-6-O-trityl- α -D-threo-hex-2-enopyranoside 3.—To a solution of compound **1** (2.30 g, 5.52 mmol), triphenylphosphine (3.90 g, 14.9 mmol) and benzoic acid (1.82 g, 14.9 mmol) in dry THF (60 cm^3), stirred at room temperature, was added dropwise diethyl azodicarboxylate (2.4 cm^3 , 14.9 mmol) over a period of 30 min. Completion was indicated by TLC (SiO_2 ; H:A 3:2) after the mixture had been stirred for 4 h. Removal of the solvent and purification by chromatography on silica gel (H:A 9:1) gave *benzoate* **3** as a crystalline solid (2.4 g, 83%), m.p. 50–52 °C (from hexane–ethyl acetate); R_f 0.66 (H:A 4:1); $[\alpha]_{\text{D}}^{20} - 178$ (c 1, CHCl_3) (Found: C, 78.6; H, 6.2. $\text{C}_{34}\text{H}_{32}\text{O}_5$ requires C, 78.44; H, 6.19%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1750 (C=O) and 1600 (C=C); δ_{H} 1.29 (3 H, t, OCH_2Me), 3.28 (1 H, dd, J_{gem} 9, $J_{5,6}$ 7, 6-H), 3.45 (1 H, dd, $J_{5,6'}$ 6.5, 6-H'), 3.60 (1 H, m, OCHHMe), 3.91 (1 H, m, OCHHMe), 4.47 (1 H, ddd, $J_{4,5}$ 2.5, 5-H), 5.08 (1 H, dd, $J_{1,2}$ 3, $J_{1,3}$ 1, 1-H), 5.30 (1 H, dd, $J_{3,4}$ 5.5, 4-H), 6.04 (1 H, dd, $J_{2,3}$ 10, 2-H), 6.28 (1 H, dd, 3-H) and 7.10–7.80 (20 H, m, Ph).

Ethyl 2,3-Dideoxy-6-O-trityl- α -D-threo-hex-2-enopyranoside 4.—A catalytic amount of sodium (11 mg, 0.46 mmol) was added to a stirred solution of the benzoate **3** (2.4 g, 4.62 mmol) in dry methanol (45 cm^3) at room temperature. TLC (SiO_2 ; H:A 2:3) indicated completion after the mixture had been stirred for 3 h. The mixture was neutralized with resin (Dowex 50W, H⁺) and filtered. The solution was then evaporated to dryness under reduced pressure and the residue was purified by column chromatography on silica gel (H:A 4:1) to give compound **4** as a crystalline solid (1.70 g, 89%), m.p. 147 °C (from hexane–ethyl acetate); R_f 0.18 (H:A, 3:1); $[\alpha]_{\text{D}}^{20} - 62$ (c 1, CHCl_3) (Found: C, 77.6; H, 6.7. $\text{C}_{27}\text{H}_{28}\text{O}_4$ requires C, 77.85; H, 6.78%); $\nu_{\text{max}}/\text{cm}^{-1}$ 3450 (OH) and 1600 (C=C); δ_{H} 1.29 (3 H, t, OCH_2Me), 1.70 (1 H, m, OH), 3.30 (1 H, dd, J_{gem} 10, $J_{5,6}$ 5, 6-H), 3.49 (1 H, dd, $J_{5,6'}$ 7, 6-H'), 3.58 (1 H, m, OCHHMe), 3.83 (1 H, br dd, $J_{3,4}$ 5, $J_{4,5}$ 2, 4-H), 3.97 (1 H, m, OCHHMe), 4.22 (1 H, ddd, 5-H), 5.05 (1 H, d, $J_{1,2}$ 3, 1-H), 5.92 (1 H, dd, $J_{2,3}$ 10.5, 2-H), 6.12 (1 H, dd, 3-H) and 7.10–7.50 (15 H, m, Ph).

Ethyl 2,3-Dideoxy-4-O-(1'-ethoxy-2'-iodoethyl)-6-O-trityl- α -D-threo-hex-2-enopyranoside 5.—Obtained as a diastereoisomeric mixture (1'S:1'R 1:1) from **4** according to general procedure B (2 mmol, 24 h; 1.15 g, 91%); R_f 0.58 (H:A, 3:1); $\nu_{\text{max}}/\text{cm}^{-1}$ 1600 (C=C); δ_{H} 1.05 (1.5 H, t, OCH_2Me), 1.16 (1.5 H, t, OCH_2Me), 1.26 (1.5 H, t, OCH_2Me), 1.30 (1.5 H, t, OCH_2Me), 2.86 (0.5 H, dd, J_{gem} 10.5, $J_{1',2'}$ 4.5, 2'-H^A), 2.96 (0.5 H, dd, $J_{1',2'}$ 4, J_{gem} 10.5, 2'-H^B), 3.00 (0.5 H, dd, $J_{1',2'}$ 6.5, 2''-H^A), 3.08

(0.5 H, dd, $J_{1',2'}$ 7, 2''-H^B), 3.19–3.31 (2 H, m, OCHHMe and 6-H), 3.41–3.64 (3 H, m, OCHHMe and 6-H'), 3.82 (1 H, ddd, $J_{4,5}$ 2.5, $J_{5,6}$ 5, $J_{5,6'}$ 6.5, 5-H), 3.89 (0.5 H, m, OCHHMe), 4.01 (0.5 H, m, OCHHMe), 4.24–4.31 (1 H, m, 4-H^A, 4-H^B), 4.63 (0.5 H, dd, 1'-H^B), 4.67 (0.5 H, dd, 1'-H^A), 5.04 (0.5 H, d, $J_{1,2}$ 2.5, 1-H^A), 5.08 (0.5 H, d, $J_{1,2}$ 2.5, 1-H^B), 5.93 (0.5 H, dd, $J_{2,3}$ 10, 2-H^A), 5.99 (0.5 H, dd, $J_{2,3}$ 10, 2-H^B), 6.09–6.14 (1 H, m, $J_{3,4}$ 5, 3-H^A, 3-H^B) and 7.15–7.50 (15 H, m, Ph).

tert-Butyl 3,4-Dideoxy-6-O-trityl- α -D-erythro-hex-3-enopyranoside 6.—*tert*-Butyl 2,4,6-tri-*O*-acetyl-3-deoxy-*D*-erythro-hex-2-enopyranoside²¹ was treated according to Isobe's method,²² followed by selective standard tritylation at C-6 to give *compound* **6** as a crystalline solid (10.42 g, 75%), m.p. 93–94 °C (from hexane–ethyl acetate); R_f 0.4 (H:A 2:1); $[\alpha]_{\text{D}}^{20} - 18.3$ (c 1, CHCl_3) (Found: C, 78.6; H, 7.3. $\text{C}_{29}\text{H}_{32}\text{O}_4$ requires C, 78.34; H, 7.26%); $\nu_{\text{max}}/\text{cm}^{-1}$ 3470 (OH) and 1600 (C=C); δ_{H} 1.55 (9 H, s, Bu^t), 2.19 (1 H, m, OH), 3.08 (1 H, dd, $J_{5,6}$ 5, J_{gem} 10, 6-H), 3.21 (1 H, dd, $J_{5,6'}$ 6.5, 6-H'), 4.15 (1 H, ddd, $J_{1,2}$ 5.5, $J_{2,3}$ 1.5, 2-H), 4.34 (1 H, ddd, $J_{4,5}$ 1.5, 5-H), 5.26 (1 H, d, 1-H), 5.69 (1 H, dd, $J_{3,4}$ 10, 3-H), 5.76 (1 H, dd, 4-H) and 7.20–7.50 (15 H, m, Ph).

tert-Butyl 3,4-Dideoxy-2-O-(1'-ethoxy-2'-iodoethyl)-6-O-trityl- α -D-erythro-hex-3-enopyranoside 7.—Obtained as a diastereoisomeric mixture (1'S:1'R 1:1) from compound **6** according to general procedure A (1 mmol, 2 h; 571 mg, 89%) and general procedure B (1 mmol, 2.5 h; 640 mg, 99%); R_f 0.5 (H:A 6:1); $\nu_{\text{max}}/\text{cm}^{-1}$ 1600 (C=C); δ_{H} 1.23 (3 H, t, OCH_2Me), 1.32 (9 H, s, Bu^t), 3.11 (0.5 H, dd, $J_{5,6}$ 2, J_{gem} 10, 6-H^A), 3.12 (0.5 H, dd, $J_{5,6}$ 2, J_{gem} 10, 6-H^B), 3.2–3.31 (3 H, m, 2'-H₂ and 6-H'), 3.60 (1 H, m, OCHHMe), 3.66 (1 H, m, OCHHMe), 4.28 (1 H, dd, $J_{1,2}$ 3.5, $J_{2,3}$ 1.5, 2-H), 4.41 (1 H, m, $J_{3,5}$ 1.5, $J_{4,5}$ 1, $J_{5,6'}$ 6, 5-H), 4.75 (0.5 H, t, $J_{1',2'}$ = $J_{1',2''}$ = 5.5, 1'-H^A), 4.82 (0.5 H, dd, $J_{1',2'}$ 4.5, $J_{1',2''}$ 6.5, 1'-H^B), 5.28 (0.5 H, d, 1-H^A), 5.29 (0.5 H, d, 1-H^B), 5.76 (1 H, dd, $J_{3,4}$ 11, 4-H), 5.83 (1 H, ddd, 3-H) and 7.20–7.50 (15 H, m, Ph).

tert-Butyl 2-O-Benzoyl-3,4-dideoxy-6-O-trityl- α -D-threo-hex-3-enopyranoside 8.—Benzoylation of alcohol **6** (3.59 g, 8 mmol) according to the Mitsunobu method as for compound **3** gave, after the mixture had been stirred for 3 h, and chromatography on silica gel (H:A 8:1), the *benzoate* **8** (3.40 g, 79%) as a foam; R_f 0.70 (H:A 4:1); $[\alpha]_{\text{D}}^{20} + 32$ (c 0.4, CHCl_3) (Found: C, 78.5; H, 6.7. $\text{C}_{36}\text{H}_{36}\text{O}_5$ requires C, 78.79; H, 6.62%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1750 (C=O) and 1600 (C=C); δ_{H} 1.25 (9 H, s, Bu^t), 3.25 (1 H, dd, $J_{5,6}$ 5.5, J_{gem} 10, 6-H), 3.35 (1 H, dd, $J_{5,6'}$ 6, 6-H'), 4.48 (1 H, m, $J_{3,5}$ 1.5, $J_{4,5}$ 1, 5-H), 5.08 (1 H, dd, $J_{1,2}$ 1.5, $J_{2,3}$ 5, 2-H), 5.33 (1 H, d, 1-H), 5.59 (1 H, ddd, $J_{3,4}$ 10, 3-H), 6.11 (1 H, dd, 4-H) and 7.20–8.10 (20 H, m, Ph).

tert-Butyl 3,4-Dideoxy-6-O-trityl- α -D-threo-hex-3-enopyranoside 9.—The benzoate **8** (3.40 g, 6.23 mmol) was subjected to a standard debenzoylation procedure as for benzoate **3** to give, after chromatography on silica gel (H:A 4:1), the *alcohol* **9** as a foam; R_f 0.35 (H:A 4:1); $[\alpha]_{\text{D}}^{20} + 11.1$ (c 0.9, CHCl_3) (Found: C, 78.1; H, 7.3. $\text{C}_{29}\text{H}_{32}\text{O}_4$ requires C, 78.34; H, 7.26%); $\nu_{\text{max}}/\text{cm}^{-1}$ 3470 (OH) and 1600 (C=C); δ_{H} 1.23 (9 H, s, Bu^t), 1.90 (1 H, br d, OH), 3.21 (1 H, dd, $J_{5,6}$ 5.5, J_{gem} 10, 6-H), 3.28 (1 H, dd, $J_{5,6'}$ 5.5, 6-H'), 3.70 (1 H, ddd, $J_{1,2}$ 2, $J_{2,3}$ 4.5, $J_{2,\text{OH}}$ 10, 2-H), 4.42 (1 H, m, $J_{4,5}$ 1.5, $J_{3,5}$ 2, 5-H), 5.07 (1 H, d, 1-H), 5.88 (1 H, dd, $J_{3,4}$ 10, 4-H), 5.99 (1 H, ddd, 3-H) and 7.20–7.50 (15 H, m, Ph).

tert-Butyl 3,4-Dideoxy-2-O-(1'-ethoxy-2'-iodoethyl)-6-O-trityl- α -D-threo-hex-3-enopyranoside 10.—Obtained as a diastereoisomeric mixture (1'S:1'R 1:1) from compound **9** according to general procedure B (0.48 mmol, 2.5 h; 230 mg, 72%); R_f 0.5 (H:A 3:1); $\nu_{\text{max}}/\text{cm}^{-1}$ 1600 (C=C); δ_{H} 1.13 (3 H, t,

OCH₂Me), 1.19 (9 H, s, Bu'), 3.08 (1 H, dd, J_{gem} 9, $J_{5,6}$ 5.5, 6-H), 3.10–3.20 (4 H, m, 2'-H₂, 6-H and OCHHMe), 3.25 (0.5 H, m, OCHHMe), 3.38 (0.5 H, m, OCHHMe), 3.59 (0.5 H, m, OCHHMe), 3.72 (0.5 H, dd, $J_{1,2}$ 2, $J_{2,3}$ 5.5, 2-H^A), 3.77 (0.5 H, dd, $J_{1,2}$ 2, $J_{2,3}$ 5.5, 2-H^B), 4.36 (1 H, m, $J_{3,5}$ 2, $J_{4,5}$ 1.5, $J_{5,6} = J_{5,6'} = 5.5$, 5-H), 4.70 (0.5 H, t, $J_{1',2'} = J_{1',2''} = 5.5$, 1'-H^A), 4.77 (0.5 H, t, $J_{1',2'} = J_{1',2''} = 5.5$, 1'-H^B), 5.07 (0.5 H, d, 1-H^A), 5.12 (0.5 H, d, 1-H^B), 5.76 (0.5 H, ddd, $J_{3,4}$ 11, 3-H^A), 5.79 (0.5 H, ddd, $J_{3,4}$ 10, 3-H^B), 5.94 (0.5 H, dd, 4-H^A), 6.00 (0.5 H, dd, 4-H^B) and 7.15–7.40 (15 H, m, Ph).

(5'R,5'S)-2,3,4-Trideoxy-5'-ethoxy-2',3',4',5'-tetrahydro-6-O-trityl-(methyl- α -D-ribo-hexopyranosido)[4,3-b]furan **11a** and **11b**.—Obtained from compound **2** according to general procedure C (0.19 mmol, 1 h; 85%); and general procedure D (0.5 mmol, 1 h; 82%); *Isomer 11a* (C: 39 mg, 42%; D: 99 mg, 40%); R_f 0.29 (H:A 6:1); $[\alpha]_D^{20} + 21.5$ (c 0.3, CHCl₃) (Found: C, 76.45; H, 7.4. C₃₁H₃₆O₅ requires C, 76.19; H, 7.43%); δ_H 1.15 (3 H, t, OCH₂Me), 1.31 (3 H, t, OCH₂Me), 1.97 (1 H, ddd, $J_{1,2e}$ 1.5, J_{gem} 13, $J_{2e,3}$ 4, 2-H^e), 2.0 (1 H, ddd, $J_{3,4}$ 9, $J_{4,5}$ 5.5, J_{gem} 15.5, 4'-H), 2.12 (1 H, ddd, $J_{3,4}$ 10, $J_{4,5}$ 6, 4'-H), 2.16 (1 H, ddd, $J_{1,2a}$ 5, $J_{2a,3}$ 8.5, 2-H^a), 2.32 (1 H, m, $J_{3,4}$ 7.5, 3-H), 3.13–3.68 (6 H, m, J_{gem} 10, 6-H₂ and 2 \times OCH₂Me), 3.88 (1 H, dd, $J_{4,5}$ 9, 4-H), 4.02 (1 H, ddd, $J_{5,6}$ 2.5, $J_{5,6}$ 5, 5-H), 4.88 (1 H, dd, 5'-H), 5.04 (1 H, dd, 1-H) and 7.2–7.5 (15 H, m, Ph). *Isomer 11b* (C: 40 mg, 43%; D: 102 mg, 42%); R_f 0.31 (H:A 6:1); $[\alpha]_D^{20} + 83.3$ (c 0.2, CHCl₃) (Found: C, 76.6; H, 7.4%); δ_H 1.13 (3 H, t, OCH₂Me), 1.25 (3 H, t, OCH₂Me), 1.63 (1 H, ddd, $J_{4,5}$ 6, $J_{3,4}$ 11, J_{gem} 15.5, 4'-H), 1.96 (1 H, ddd, $J_{1,2a}$ 5, J_{gem} 13, $J_{2a,3}$ 8, 2-H^a), 2.01 (1 H, ddd, $J_{4,5}$ 5.5, $J_{3,4}$ 9.5, 4'-H), 2.03 (1 H, ddd, $J_{1,2e}$ 1.5, $J_{2e,3}$ 5, 2-H^e), 2.43 (1 H, m, $J_{3,4}$ 7.5, 3-H), 3.20–3.30 (2 H, m, J_{gem} 9, 6-H and OCHHMe), 3.37 (1 H, m, OCHHMe), 3.5 (1 H, m, OCHHMe), 3.63 (1 H, m, OCHHMe), 3.8 (1 H, ddd, $J_{4,5}$ 9, $J_{5,6}$ 3, $J_{5,6}$ 5.5, 5-H), 3.91–4.0 (2 H, m, 4- and 6-H), 4.88 (1 H, dd, 5'-H), 5.08 (1 H, dd, 1-H) and 7.20–7.50 (15 H, m, Ph).

(5'R,5'S)-2,3,4-Trideoxy-5'-ethoxy-2',3',4',5'-tetrahydro-6-O-trityl(ethyl α -D-lyxo-hexopyranosido)[4,3-b]furan **12a** and **12b**.—Obtained from compound **5** according to general procedure D (1 mmol, 1 h; 96%); *Isomer 12a* (242 mg, 50%); R_f 0.55 (H:A 4:1); $[\alpha]_D^{20} + 16.9$ (c 1, CHCl₃) (Found: C, 76.5; H, 7.5. C₃₁H₃₆O₅ requires C, 76.19; H, 7.43%); δ_H 1.12 (3 H, m, OCH₂Me), 1.23 (3 H, m, OCH₂Me), 1.58 (1 H, ddd, $J_{1,2e}$ 2, J_{gem} 14, $J_{2e,3}$ 6.5, 2-H^e), 1.67 (1 H, dd, $J_{4,5}$ 1, J_{gem} 14, 4'-H), 2.09 (1 H, ddd, $J_{1,2a}$ 4, $J_{2a,3}$ 11, 2-H^a), 2.13 (1 H, ddd, $J_{4,5}$ 6.5, $J_{3,4}$ 6, 4'-H), 2.37 (1 H, m, $J_{3,4}$ 7, 3-H), 3.37 (1 H, m, OCHHMe), 3.38 (1 H, d, $J_{5,6}$ 6, 6-H₂), 3.47 (1 H, m, OCHHMe), 3.66 (1 H, m, OCHHMe), 3.79 (1 H, m, OCHHMe), 3.81 (1 H, dd, $J_{4,5}$ 2, 4-H), 3.95 (1 H, dt, 5-H), 4.86 (1 H, dd, 1-H), 5.05 (1 H, dd, 5'-H) and 7.10–7.60 (15 H, m, Ph). *Isomer 12b* (224 mg, 46%); R_f 0.48 (H:A 4:1); $[\alpha]_D^{20} - 20.4$ (c 1, CHCl₃) (Found: C, 75.9; H, 7.45%); δ_H 1.10 (3 H, m, OCH₂Me), 1.30 (3 H, m, OCH₂Me), 1.5 (1 H, ddd, $J_{1,2a}$ 3.5, J_{gem} 14, $J_{2a,3}$ 10, 2-H^a), 1.63 (1 H, ddd, $J_{1,2e}$ 3.5, $J_{2e,3}$ 6.5, 2-H^e), 1.85 (1 H, ddd, $J_{4,5}$ 5.5, $J_{3,4}$ 2.5, J_{gem} 13, 4'-H), 1.93 (1 H, ddd, $J_{4,5}$ 3.5, $J_{3,4}$ 7, 4'-H), 2.55 (1 H, m, $J_{3,4}$ 5, 3-H), 3.30 (1 H, dd, $J_{5,6}$ 6, J_{gem} 9, 6-H), 3.37 (1 H, dd, $J_{5,6}$ 6, 6-H), 3.40 (1 H, m, OCHHMe), 3.47 (1 H, m, OCHHMe), 3.68 (1 H, m, OCHHMe), 3.79 (1 H, m, OCHHMe), 3.99–4.04 (2 H, m, $J_{4,5}$ 2, 4- and 5-H), 4.82 (1 H, dd, 1-H), 5.16 (1 H, dd, 5'-H) and 7.10–7.50 (15 H, m, Ph).

(5'R,5'S)-2,3,4-Trideoxy-5'-ethoxy-2',3',4',5'-tetrahydro-6-O-trityl-(tert-butyl- α -D-ribo-hexopyranosido)[2,3-b]furan **13a** and **13b**.—Obtained from compound **7** according to general procedure C (0.28 mmol, 30 min; 89%); *Isomer 13a* (65 mg, 45%); R_f 0.36 (H:A 6:1); $[\alpha]_D^{20} + 29.5$ (c 0.7, CHCl₃) (Found: C, 76.3; H, 7.8. C₃₃H₄₀O₅ requires C, 76.70; H, 7.81%); δ_H 1.2 (3 H, t, OCH₂Me), 1.27 (9 H, s, Bu'), 1.57–1.65 (2 H, m, 4-H₂), 1.98 (1 H,

ddd, J_{gem} 12.5, $J_{4',5'}$ 5, $J_{3,4}$ 7.5, 4'-H), 2.12 (1 H, dt, $J_{4',5'}$ 6.5, $J_{3,4}$ 12.5, 4'-H), 2.43 (1 H, m, $J_{2,3}$ 7, $J_{3,4a}$ 9, $J_{3,4e}$ 3, 3-H), 2.97 (1 H, dd, $J_{5,6}$ 4.5, J_{gem} 9.5, 6-H), 3.18 (1 H, dd, $J_{5,6}$ 6.5, 6-H), 3.47 (1 H, m, OCHHMe), 3.84 (1 H, m, OCHHMe), 3.94 (1 H, dd, $J_{1,2}$ 5, 2-H), 4.25 (1 H, m, $J_{4a,5}$ 9.5, $J_{4e,5}$ 2, 5-H), 5.07 (1 H, d, 1-H), 5.20 (1 H, d, 5'-H) and 7.20–7.47 (15 H, m, Ph); *Isomer 13b* (63 mg, 44%) obtained as a crystalline solid, m.p. 141 °C (from hexane-ethyl acetate); R_f 0.43 (H:A 6:1); $[\alpha]_D^{20} - 12$ (c 0.8, CHCl₃) (Found: C, 76.4; H, 7.8%); δ_H 1.2 (3 H, t, OCH₂Me), 1.27 (9 H, s, Bu'), 1.59–1.60 (2 H, m, J_{gem} 12, 4-H₂), 1.64 (1 H, dd, $J_{3,4}$ 8, J_{gem} 12.5, 4'-H), 2.34 (1 H, dt, $J_{4',5'}$ 6, $J_{3,4}$ 12.5, 4'-H), 2.59 (1 H, m, $J_{2,3}$ 7.5, $J_{3,4e}$ 3.5, $J_{3,4a}$ 7.5, 3-H), 2.95 (1 H, dd, $J_{5,6}$ 4.5, J_{gem} 9.5, 6-H), 3.18 (1 H, dd, $J_{5,6}$ 6.5, 6-H), 3.44 (1 H, m, OCHHMe), 3.74 (1 H, m, OCHHMe), 4.10 (1 H, dd, $J_{1,2}$ 5, 2-H), 4.16 (1 H, m, $J_{4a,5}$ 7.5, $J_{4e,5}$ 4, 5-H), 5.06 (1 H, d, 1-H), 5.20 (1 H, d, 5'-H) and 7.20–7.50 (15 H, m, Ph).

(5'R,5'S)-2,3,4-Trideoxy-5'-ethoxy-2',3',4',5'-tetrahydro-6-O-trityl-(tert-butyl- α -D-lyxo-hexopyranosido)[2,3-b]furan **14a** and **14b**.—Obtained from compound **10** according to general procedure D (0.36 mmol, 3 h; 82%); *Isomer 14a* (77 mg, 42%) obtained as a crystalline solid, m.p. 116 °C (from hexane-ethyl acetate); R_f 0.54 (H:A 3:1); $[\alpha]_D^{20} + 44.3$ (c 0.9, CHCl₃) (Found: C, 76.4; H, 7.65. C₃₃H₄₀O₅ requires C, 76.70; H, 7.81%); δ_H 0.98 (1 H, q, $J_{3,4a} = J_{gem} = J_{4a,5} = 13$, 4-H^a), 1.18 (3 H, t, OCH₂Me), 1.29 (9 H, s, Bu'), 1.55 (1 H, ddd, $J_{3,4e}$ 6.5, J_{gem} 13.5, $J_{4e,5}$ 2.5, 4-H^e), 1.80–1.85 (2 H, m, 4'-H₂), 2.35 (1 H, m, $J_{2,3}$ 3.5, $J_{3,4'} = J_{3,4''} = 6$, 3-H), 2.79 (1 H, dd, $J_{5,6}$ 5.5, J_{gem} 9, 6-H), 3.14 (1 H, dd, $J_{5,6}$ 6.5, 6-H), 3.38 (1 H, m, OCHHMe), 3.62 (1 H, d, 2-H), 3.72 (1 H, m, OCHHMe), 4.03 (1 H, m, 5-H), 5.11 (1 H, t, $J_{4',5'} = J_{4'',5''} = 5$, 5'-H), 5.16 (1 H, s, 1-H) and 7.10–7.40 (15 H, m, Ph). *Isomer 14b* (74 mg, 40%); R_f 0.46 (H:A 3:1); $[\alpha]_D^{20} - 14.8$ (c 1, CHCl₃) (Found: C, 76.35; H, 7.7%); δ_H 1.16 (3 H, t, OCH₂Me), 1.28 (9 H, s, Bu'), 1.50 (1 H, ddd, J_{gem} 13, $J_{3,4e}$ 6, $J_{4e,5}$ 2, 4-H^e), 1.71 (1 H, d, J_{gem} 13, 4'-H), 1.78 (1 H, q, $J_{3,4a} = J_{4a,5} = 13$, 4-H^a), 2.12 (1 H, ddd, $J_{4',5'}$ 6, $J_{3,4'}$ 7, 4'-H), 2.32 (1 H, m, $J_{2,3}$ 3.5, 3-H), 2.97 (1 H, dd, $J_{5,6}$ 5, J_{gem} 9, 6-H), 3.20 (1 H, dd, $J_{5,6}$ 6, 6-H), 3.37 (1 H, m, OCHHMe), 3.59 (1 H, dd, $J_{1,2}$ 1, 2-H), 3.78 (1 H, m, OCHHMe), 4.06 (1 H, m, 5-H), 5.07 (1 H, d, 4'-H), 5.23 (1 H, d, 1-H) and 7.15–7.50 (15 H, m, Ph).

1'-Ethoxy-2'-iodoethyl 4,6-Di-O-acetyl-2,3-dideoxy- α , β -D-erythro-hex-2-enopyranoside **17**.—Obtained as a diastereoisomeric mixture (α 1'S: α 1'R: β 1'S: β 1'R 1.5:1.5:0.5:0.5) from compound **16**²³ according to general procedure A (5 mmol, 48 h; 1.92 g, 90%) and general procedure B (1 mmol, 2 h; 405 mg, 95%); R_f 0.5 (H:A 3:1); ν_{max}/cm^{-1} 1750 (C=O) and 1600 (C=C); δ_H α -anomers 1.22–1.28 (3 H, m, OCH₂Me), 2.09–2.14 (6 H, m, OAc), 3.29–3.34 (2 H, m, J_{gem} 10, 2'-H^A, 2'-H^B, 2''-H^A, 2''-H^B), 3.55–3.80 (2 H, m, OCH₂Me), 4.14–4.26 (3 H, m, $J_{5,6}$ 2, $J_{5,6}$ 5, J_{gem} 9.5, 5-H^A, 5-H^B, 6-H^A, 6-H^B), 4.85 (0.5 H, t, $J_{1',2'}$ = $J_{1',2''}$ = 5, 1'-H^A), 4.88 (0.5 H, t, $J_{1',2'}$ = $J_{1',2''}$ = 5, 1'-H^B), 5.29 (0.5 H, dd, $J_{2,4}$ 2, $J_{4,5}$ 9, 4-H^A), 5.31 (0.5 H, dd, $J_{1,2}$ 2.5, $J_{1,3}$ 1, 1-H^A), 5.32 0.5 H, dd, $J_{2,4}$ 2, $J_{4,5}$ 9, 4-H^B), 5.36 (0.5 H, dd, $J_{1,2}$ 2.5, $J_{1,3}$ 1, 1-H^B), 5.83 (0.5 H, ddd, $J_{2,3}$ 10, 2-H^A), 5.86 (0.5 H, ddd, $J_{2,3}$ 10, 2-H^B), 5.94 (0.5 H, dd, 3-H^A) and 5.96 (0.5 H, dd, 3-H^B); β -anomers 4.87 (0.5 H, t, $J_{1',2'}$ = $J_{1',2''}$ = 5, 1'-H^A), 4.93 (0.5 H, t, $J_{1',2'}$ = $J_{1',2''}$ = 6, 1'-H^B) and 5.41–5.44 (1 H, m, $J_{1,2}$ 2, 1-H^A, 1-H^B).

2'-Bromo-1'-ethoxyethyl 4,6-Di-O-acetyl-2,3-dideoxy- α , β -D-erythro-hex-2-enopyranoside **18**.—Obtained as a diastereoisomeric mixture (α 1'S: α 1'R: β 1'S: β 1'R 1.5:1.5:0.5:0.5) from compound **16** according to general procedure B (1 mmol, 15 min; 378 mg, 99%); R_f 0.5 (H:A 3:1); ν_{max}/cm^{-1} 1740 (C=O) and 1600 (C=C); δ_H α -anomers (1'S:1'R 1:1) 1.23–1.28 (3 H, m, OCH₂Me), 2.08–2.13 (6 H, m, OAc), 3.39–3.52 (2 H, m, J_{gem} 10, 2'-H^A, 2'-H^B), 3.57–3.70 (2 H, m, OCH₂Me), 4.16–4.26 (3 H, m, 5-H^A, 5-H^B, 6-H^A, 6-H^B), 4.91 (0.5 H, t, $J_{1',2'}$ = $J_{1',2''}$ = 5.5,

1'-H^A), 4.97 (0.5 H, t, $J_{1',2'} = J_{1',2''} = 5.5$, 1'-H^B), 5.30 (0.5 H, dd, $J_{2,4}$ 2, $J_{4,5}$ 9.5, 4-H^A), 5.31 (0.5 H, dd, $J_{1,2}$ 2.5, $J_{1,3}$ 1, 1-H^A), 5.33 (0.5 H, dd, $J_{2,4}$ 2, $J_{4,5}$ 9.5, 4-H^B), 5.40 (0.5 H, dd, $J_{1,2}$ 2.5, $J_{1,3}$ 1, 1-H^B), 5.82 (0.5 H, ddd, $J_{2,3}$ 10, 2-H^A), 5.86 (0.5 H, ddd, $J_{2,3}$ 10, 2-H^B), 5.93 (0.5 H, dd, 3-H^A) and 5.96 (0.5 H, dd, 3-H^B); β -anomers 4.89 (0.5 H, t, $J_{1',2'} = J_{1',2''} = 4$, 1'-H^A), 5.06 (0.5 H, dd, $J_{1',2'} = 4$, $J_{1',2''} = 6$, 1'-H^B) and 5.42–5.46 (1 H, m, $J_{1,2}$ 2, 1-H^A, 1-H^B).

Compounds **19**, **30** and **35** were obtained from either iodide **17** or bromide **18**. Iodo acetal **17** was subjected to general procedure C (0.28 mmol) to give compounds **19** (diastereoisomeric mixture, 26 mg, 31%), **30** (diastereoisomeric mixture, 2'R:2'S 1:1, 42 mg, 50%) and **35** (β -anomer 2'S, 14 mg, 6%) or to general procedure D (1 mmol) to give compounds **19** (diastereoisomeric mixture, 48 mg, 16%), **30** (diastereoisomeric mixture, 2'R:2'S 1:1, 202 mg, 67%) and **35** (β -anomer 2'S, 48 mg, 16%). The bromo acetal **18** (0.48 mmol) was subjected to general procedure D to give compounds **19** (diastereoisomeric mixture, 8 mg, 5%), **30** (diastereoisomeric mixture, 2'R:2'S 1:1, 98 mg, 68%) and **35** (β -anomer 2'S, 37 mg, 25%).

1'-Ethoxyethyl 4,6-Di-O-acetyl-2,3-dideoxy- α,β -D-erythro-hex-2-enopyranoside **19**. R_f 0.42 (H:A 3:1); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O) and 1600 (C=C); δ_{H} 1.15–1.40 (6 H, m, OCH₂Me, Me), 1.99–2.06 (6 H, m, 2 \times OAc), 3.44–3.57 (1 H, m, OCHHMe), 3.76–3.86 (1 H, m, OCHHMe), 4.10–4.27 (3 H, m, 5-H and 6-H₂), 4.87–4.97 (1 H, m, 4-H), 5.22–5.33 (2 H, m, 1- and 1'-H) and 5.75–5.96 (2 H, m, 2- and 3-H).

4,6-Di-O-acetyl-1,2,3-trideoxy-5'-ethoxy-2',3',4',5'-tetrahydro- α,β -D-ribo-hexopyranosyl[1,2-b]furan **30**. R_f 0.37 (H:A 3:1) (Found: C, 55.5; H, 7.4. C₁₄H₂₂O₇ requires C, 55.60; H, 7.34%); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O); δ_{H} 1.2 (1.5 H, t, OCH₂Me), 1.25 (1.5 H, t, OCH₂Me), 1.5 (0.5 H, dt, $J_{2,3a} = J_{3a,4} = 9$, J_{gem} 13.5, 3-H^A), 2.0 (0.5 H, dd, $J_{2,4}$ 3.5, J_{gem} 8, 4'-H^A), 2.02–2.18 (9.5 H, m, 2 \times OAc, 2-H^A, 3-H^{Ae}, 3-H^{Be}, 4'-H^B and 4'-H^A, 3-H^{Ba}, 4'-H₂^B), 2.47 (0.5 H, m, $J_{1,2}$ 3.5, $J_{2,3e}$ 3, $J_{2,3'}$ 11, 2-H^B), 3.48 (1 H, m, OCHHMe), 3.83 (1 H, m, OCHHMe), 3.96 (0.5 H, ddd, $J_{4,5}$ 8.5, $J_{5,6}$ 2.5, $J_{5,6}$ 5, 5-H^A), 4.03 (0.5 H, ddd, $J_{4,5}$ 8.5, $J_{5,6}$ 2.5, $J_{5,6}$ 5, 5-H^B), 4.15 (1 H, dd, J_{gem} 11.5, 6-H), 4.28 (0.5 H, dd, 6-H^A), 4.36 (0.5 H, dd, 6-H^B), 4.78 (0.5 H, ddd, $J_{3e,4e}$ 5, 4-H^A), 4.82 (0.5 H, ddd, $J_{3e,4}$ 5, 4-H^B), 5.08 (0.5 H, d, $J_{4',5'}$ 6, 5'-H^A), 5.28 (0.5 H, dd, $J_{4',5'}$ 4, $J_{4',5'}$ 5.5, 5'-H^B), 5.41 (0.5 H, d, 1-H^B) and 5.50 (0.5 H, d, 1-H^A).

(5'S)-4,6-Di-O-acetyl-1,2,3-trideoxy-5'-ethoxy-2',3',4',5'-tetrahydro- β -D-arabino-hexopyranosyl[1,2-b]furan **35**. R_f 0.27 (H:A 3:1); $[\alpha]_{\text{D}}^{20} - 10.3$ (c 1.6, CHCl₃) (Found: C, 55.9; H, 7.4%); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O); δ_{H} 1.22 (3 H, t, OCH₂Me), 1.80 (1 H, ddd, $J_{2,3a}$ 6, J_{gem} 13.5, $J_{3a,4}$ 8, 3-H^A), 1.95 (1 H, ddd, $J_{2,4}$ 10, $J_{4',5'}$ 5.5, J_{gem} 12.5, 4'-H), 2.05 (3 H, s, OAc), 2.08 (3 H, s, OAc), 2.19 (1 H, ddd, $J_{2,4}$ 8.5, $J_{4',5'}$ 5.5, 4'-H), 2.24 (1 H, td, $J_{2,3e} = J_{3e,4} = 5$, 3-H^e), 2.38 (1 H, m, $J_{1,2}$ 3, 2-H), 3.51 (1 H, m, OCHHMe), 3.63 (1 H, ddd, $J_{4,5}$ 8.5, $J_{5,6}$ 5.5, $J_{5,6}$ 2.5, 5-H), 3.87 (1 H, dq, OCHHMe), 4.17 (1 H, dd, J_{gem} 11.5, 6-H), 4.27 (1 H, dd, 6-H), 4.95 (1 H, ddd, 4-H), 5.17 (1 H, d, 1-H) and 5.24 (1 H, t, 5'-H).

2'-Iodoethyl 4,6-Di-O-acetyl-2,3-dideoxy- α,β -D-erythro-hex-2-enopyranoside **20**.—Obtained as an anomeric mixture ($\alpha:\beta$ 7:1) according to general procedure F (1.5 mmol; 573 mg; 99%), R_f 0.3 (H:A 3:1); $[\alpha]_{\text{D}}^{20} + 68.7$ (c 1.4, CHCl₃) (Found: C, 37.75; H, 4.5; I, 33.1. C₁₂H₁₇IO₆ requires C, 37.50; H, 4.46; I, 33.04%); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O) and 1605 (C=C); δ_{H} 2.09 (3 H, s, OAc), 2.12 (3 H, s, OAc), 3.52–3.58 (2 H, m, 2'-H₂), 3.92 (1 H, ddd, J_{gem} 11, $J_{1',2'}$ 5.5, $J_{1',2''}$ 6.5, 1'-H), 4.05 (1 H, ddd, $J_{1',2'}$ 5.5, $J_{1',2''}$ 6.5, 1'-H), 4.17 (1 H, ddd, $J_{4,5}$ 9, $J_{5,6}$ 2.5, $J_{5,6}$ 5, 5-H), 4.21–4.26 (2 H, m, J_{gem} 10, 6-H₂), 5.09 (0.87 H, dd, $J_{1,2}$ 2, $J_{1,3}$ 1, 1-H^A), 5.20 (0.13 H, dd, 4-H^B), 5.21 (0.13 H, dd, 1-H^B), 5.32 (0.87 H, dd, $J_{2,4}$ 1.5, 4-H^A), 5.86 (0.87 H, ddd, $J_{2,3}$ 10, 2-H^A), 5.92 (0.87 H, dd, 3-H^A), 5.97 (0.13 H, dd, $J_{2,3}$ 10, 2-H^B) and 6.02 (0.13 H, ddd, 3-H^B).

Compounds **15** and **33** were obtained from either substrate **20**

or **21** according to general procedure C or E. 4,6-Di-O-acetyl-1,2,3-trideoxy-2',3',4',5'-tetrahydro- α,β -D-ribo-hexopyranosyl[1,2-b]furan **33**: ($\alpha:\beta$ 9.3:0.7, 219 mg, 84%); m.p. 66 °C (from hexane); R_f 0.36 (H:A 3:1); $[\alpha]_{\text{D}}^{20} + 97.3$ (c 0.9, CHCl₃) {lit.,^{11e} m.p. 69–71.5 °C; $[\alpha]_{\text{D}} + 102$ (CHCl₃)}.

Compound **21** (1 mmol) treated with tributyltin deuteride according to general procedure C gave products **22** and **36**. 2-Deuterioethyl 4,6-di-O-acetyl-2,3-dideoxy- α,β -D-erythro-hex-2-enopyranoside **22**: (15 mg, 6%), R_f 0.65 (H:A 3:2); $[\alpha]_{\text{D}}^{20} + 12.4$ (c 0.9, CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O) and 1600 (C=C); δ_{H} 1.26 (2 H, t, J_{8} , OCH₂CH₂D), 2.08 (3 H, s, OAc), 2.10 (3 H, s, OAc), 3.58 (1 H, m, J_{gem} 14, OCHHCH₂D), 3.82 (1 H, m, OCHHCH₂D), 4.11 (1 H, ddd, $J_{4,5}$ 10, $J_{5,6}$ 2.5, $J_{5,6}$ 5.5, 5-H), 4.17 (1 H, dd, J_{gem} 12, 6-H), 4.25 (1 H, dd, 6H), 5.05 (1 H, dd, $J_{1,2}$ 2, $J_{1,3}$ 1, 1-H), 5.31 (1 H, dd, $J_{3,4}$ 2, 4-H), 5.84 (1 H, ddd, $J_{2,3}$ 10, 3-H) and 5.88 (1 H, dd, 2-H).

4,6-Di-O-acetyl-1,2,3-trideoxy-3-deuterio-2',3',4',5'-tetrahydro- α,β -D-glucopyranosyl[1,2-b]furan **36**: ($\alpha:\beta$ 9.3:0.7, 219 mg, 84%) R_f 0.37 (H:A 3:2); $[\alpha]_{\text{D}}^{20} + 91.7$ (c 0.4, CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O); δ_{H} 1.48 (1 H, t, $J_{2,3a} = J_{3a,4} = 10$, 3-H^A), 1.77 (1 H, m, $J_{2,4}$ 2.5, $J_{4',5'}$ 3.5, J_{gem} 10, 4'-H), 2.05 (3 H, s, OAc), 2.08 (3 H, s, OAc), 2.15 (1 H, m, $J_{2,4}$ 7, $J_{4',5'}$ 9, 4'-H), 2.32 (1 H, m, $J_{1,2}$ 3.5, $J_{2,3a}$ 10, 2-H), 3.62 (0.07 H, ddd, 5-H^B), 3.89 (1 H, ddd, J_{gem} 8.5, $J_{4',5'}$ 3.5, 5'-H), 3.92 (0.93 H, ddd, $J_{4,5}$ 10, $J_{5,6}$ 2.5, $J_{5,6}$ 5, 5-H^A), 4.09–4.16 (2 H, m, 6- and 5'-H), 4.30 (1 H, dd, J_{gem} 12, 6-H'), 4.77 (1 H, t, 4-H), 5.12 (0.07 H, d, 1-H^B) and 5.30 (0.93 H, d, H-1^A).

3'-Bromopropyl 4,6-Di-O-acetyl-2,3-dideoxy- α,β -D-erythro-hex-2-enopyranoside **23**.—Obtained as an anomeric mixture ($\alpha:\beta$ 9:1) according to general procedure F (2 mmol, 5 min; 696 mg, 99%), R_f 0.3 (H:A 4:1); $[\alpha]_{\text{D}}^{20} + 88.5$ (c 1.5, CHCl₃) (Found: C, 44.5; H, 5.5; Br, 22.9. C₁₃H₁₆BrO₆ requires C, 44.44; H, 5.45; Br, 22.76%); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O) and 1600 (C=C); δ_{H} 2.08–2.20 (8 H, m, 2 OAc, 2'-H₂), 3.49–3.57 (2 H, m, 3'-H₂), 3.63 (1 H, ddd, $J_{1',2'}$ 5, $J_{1',2''}$ 6, J_{gem} 10, 1'-H), 3.96 (1 H, ddd, $J_{1',2'}$ 5, $J_{1',2''}$ 7, 1'-H), 4.19 (1 H, ddd, $J_{4,5}$ 9.5, $J_{5,6}$ 2.5, $J_{5,6}$ 5.5, 5-H), 4.20 (1 H, dd, J_{gem} 11, 6-H), 4.26 (1 H, dd, 6-H'), 5.05 (0.9 H, dd, $J_{1,2}$ 3.5, $J_{1,3}$ 1, 1-H^A), 5.15 (0.1 H, dd, $J_{1,2}$ 1.5, 1-H^B), 5.20 (0.1 H, ddd, 4-H^B), 5.32 (0.9 H, dd, $J_{2,4}$ 2, 4-H^A), 5.83 (0.9 H, ddd, $J_{2,3}$ 10.5, 2-H^A), 5.90 (0.9 H, dd, 3-H^A), 5.93 (0.1 H, dd, 3-H^B) and 5.99 (0.1 H, ddd, 2-H^B).

Propyl 4,6-Di-O-acetyl-2,3-dideoxy- α,β -D-erythro-hex-2-enopyranoside **24**.—Obtained from the bromo derivative **23** according to general procedure C (1 mmol; 270 mg, 99%) or general procedure D (0.5 mmol; 136 mg, 99%), R_f 0.5 (H:A, 3:1); $[\alpha]_{\text{D}}^{20} + 92$ (c 1, CHCl₃) {lit.,¹³ $[\alpha]_{\text{D}}^{20} + 96$ (c 1, CHCl₃)}.

4,6-Di-O-acetyl-1-O-(bromoacetyl)-2,3-dideoxy- α,β -D-erythro-hex-2-enopyranoside **25**.—To a solution of the hemiacetal **16** (229 mg, 1 mmol) in methylene dichloride (5 cm³) containing triethylamine (0.2 cm³, 1.5 mmol) was added dropwise bromoacetyl bromide (0.13 cm³, 1.5 mmol) at room temperature. After the mixture had been stirred for 2 h, extraction with methylene dichloride, washing of the extract with water, drying (MgSO₄) and concentration under reduced pressure gave a residue, which was filtered through silica gel to give the bromoacetate **25** (400 mg, 99%) R_f 0.73 (H:A 1:1); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O) and 1605 (C=C).

The crude bromoacetate was treated according to general procedure C to give 1,4,6-tri-O-acetyl-2,3-dideoxy- α,β -D-erythro-hex-2-enopyranoside **26**: ($\alpha:\beta$ 7:3, 138 mg, 51%), identical with an authentic sample prepared by acetylation of compound **16**.

2'-Bromoethyl 2,4,6-Tri-O-acetyl-3-deoxy- α,β -D-erythro-hex-2-enopyranoside **27**.—Obtained according to general procedure F (3 mmol, 30 min; 1.146 g, 96%), R_f 0.45 (H:A, 3:2); $[\alpha]_{\text{D}}^{20} + 80.2$

(c 1, CHCl₃) (Found: C, 42.7; H, 4.9; Br, 20.3. C₁₄H₁₉BrO₈ requires C, 42.53; H, 4.85; Br, 20.23%); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O) and 1705 (C=C); δ_{H} 2.02 (6 H, s, 2 × OAc), 2.10 (3 H, s, OAc), 3.48 (2 H, t, *J*_{6,2'} 6, 2'-H₂), 3.84 (1 H, dt, *J*_{gem} 11.5, 1'-H), 3.96 (1 H, dt, 1'-H), 4.02 (1 H, m, *J*_{4,5} 8, *J*_{5,6} = *J*_{5,6} = 2.5, 5-H), 4.10–4.16 (2 H, m, 6-H₂), 5.07 (1 H, s, 1-H), 5.35 (1 H, dd, *J*_{3,4} 2, 4-H) and 5.65 (1 H, d, 3-H).

Compound **27** (1.43 mmol) was treated according to procedure D to give the known compound **28** and the new compound **34**. Ethyl 2,4,6-tri-*O*-acetyl-3-deoxy- α -D-erythro-hex-2-enopyranoside **28** (110 mg, 24%); *R*_f 0.44 (H:E 1:4); [α]_D²⁰ +88.1 (c 1, CHCl₃) {lit.,²⁴ [α]_D²⁰ +45}; 2,4,6-Tri-*O*-acetyl-1,3-dideoxy-2',3',4',5'-tetrahydro- α -D-arabino-hexopyranosyl[1,2-*b*]furan **34**: (260 mg, 57%); *R*_f 0.27 (H:E 1:4); [α]_D²⁰ +39.8 (c 0.9, CHCl₃) (Found: C, 53.3; H, 6.3. C₁₄H₂₀O₈ requires C, 53.14; H, 6.38%); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O); δ_{H} 2.02–2.08 (4 H, m, OAc, 3-H^a), 2.09 (6 H, s, 2 × OAc), 2.32 (1 H, ddd, *J*_{4',5'} 8, *J*_{4',5'} 8, *J*_{4',5'} 8.5, *J*_{gem} 13,4'-H), 2.59 (1 H, ddd, *J*_{4',5'} 8, *J*_{4',5'} 6, 4'-H), 2.71 (1 H, dd, *J*_{gem} 14.5, *J*_{3e,4} 5, 3-H^a), 4.00–4.12 (3 H, m, *J*_{gem} 13, 5'-H₂ and 5-H), 4.19 (1 H, dd, *J*_{gem} 12, *J*_{5,6} 2.5, 6-H), 4.30 (1 H, dd, *J*_{5,6} 5.5, 6-H¹), 4.93 (1 H, dt, *J*_{3a,4} = *J*_{4,5} = 8, 4-H) and 5.25 (1 H, s, 1-H).

Compound **27** (1 mmol) was treated with tributyltin deuteride according to general procedure C to give products **29** and **37**. 2'-Deuterioethyl 2,4,6-tri-*O*-acetyl-3-deoxy- α -D-erythro-hex-2-enopyranoside **29**: (104 mg, 32%); *R*_f 0.53 (H:A 3:2); [α]_D²⁰ +57.5 (c 1, CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O) and 1705 (C=C); δ_{H} 1.25 (2 H, t, OCH₂CH₂D), 2.10 (3 H, s, OAc), 2.12 (3 H, s, OAc), 2.19 (3 H, s, OAc), 3.92 (1 H, dt, *J*_{gem} 11.5, 1'-H), 4.05 (1 H, dt, 1'-H), 4.12 (1 H, ddd, *J*_{4,5} 9, *J*_{5,6} 7, *J*_{5,6} 3, 5-H), 4.20–4.25 (2 H, m, 6-H₂), 5.15 (1 H, s, 1-H), 5.46 (1 H, dd, *J*_{3,4} 2, 4-H) and 5.75 (1 H, d, 3-H).

2,4,6-Tri-*O*-acetyl-1,3-dideoxy-3-deuterio-2',3',4',5'-tetrahydro- α -D-mannopyranosyl[1,2-*b*]furan **37**: (320 mg, 62%); *R*_f 0.42 (H:A 3:2); [α]_D²⁰ +28.4 (c 1, CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ 1750 (C=O); δ_{H} 2.00–2.10 (10 H, m, 3 × OAc, 3-H^a), 2.32 (1 H, ddd, *J*_{4',5'} 8, *J*_{4',5'} 8, *J*_{gem} 13.5, 4'-H), 2.58 (1 H, ddd, *J*_{4',5'} 8, *J*_{4',5'} 5, 4'-H), 4.00–4.12 (3 H, m, *J*_{gem} 14, 5'-H₂ and 5-H), 4.19 (1 H, dd, *J*_{5,6} 3, *J*_{gem} 12, 6-H), 4.30 (1 H, dd, *J*_{5,6} 6, 6-H¹), 4.93 (1 H, t, *J*_{3a,4} = *J*_{4,5} = 8.5, 4-H) and 5.24 (1 H, s, 1-H).

4,6-Di-*O*-acetyl-1,2,3-trideoxy-2',3',4',5'-tetrahydro-5'-oxo- α -D-ribo-hexopyranosyl[1,2-*b*]furan **32**.—A solution of the acetal **30** (191 mg, 0.63 mmol) in aq. 1,4-dioxane (10 cm³; 1:1) containing a catalytic amount of 0.1 mol dm⁻³ acetic acid (0.06 mmol) was heated under reflux for 6 h. 0.1 mol dm⁻³ Sodium hydroxide was then added, the solvent was removed, and the residue was coevaporated with ethanol under reduced pressure to give the hemiacetal **31** as an oil; *R*_f 0.15 (H:A 1:1); $\nu_{\max}/\text{cm}^{-1}$ 3240 (OH) and 1750 (C=O).

Crude compound **31** was dissolved in methylene dichloride (3 cm³) and added dropwise to a solution of methylene dichloride (5 cm³) containing NIS (292 mg, 3.05 mmol) and tetrabutylammonium iodide (96 mg, 0.63 mmol) at room temperature. The reaction mixture was stirred for 4 h at the same temperature. Then a saturated solution of sodium thiosulfate was added, the mixture was extracted with methylene dichloride and the extract was washed with water, dried (Na₂SO₄), and evaporated to dryness to give a gum, which was purified by chromatography on silica gel (H:A 1:1) to give title compound **32** (170 mg, 99%); *R*_f 0.3 (H:A 1:1); [α]_D²⁰ +32.2 (c 0.9, CHCl₃) (Found: C, 52.75; H, 5.7. C₁₂H₁₆O₇ requires C, 52.92; H, 5.93%); $\nu_{\max}/\text{cm}^{-1}$ 1785 (C=O, lactone) and 1750 (C=O, ester); δ_{H} 1.52 (1 H, dt, *J*_{2,3a} = *J*_{3a,4} = 8.5, *J*_{gem} 13.5, 3-H^a), 2.07 (3 H, s, OAc), 2.10 (3 H, s, OAc), 2.28 (1 H, ddd, *J*_{2,3e} 6.5, *J*_{3e,4} 4.5, 3-H^a), 2.45 (1 H, d, *J*_{gem} 15, 4'-H), 2.87 (1 H, m, *J*_{1,2} 4.5, *J*_{2,4'} 7.5, 2-H), 2.92 (1 H, dd, 4'-H), 3.98 (1 H, ddd, *J*_{4,5} 9, *J*_{5,6} 2.5, *J*_{5,6} 5, 5-H), 4.20 (1 H, dd, *J*_{gem} 11.5, 6-H), 4.30 (1 H, dd, 6-H¹), 4.88 (1 H, ddd, 4-H) and 5.95 (1 H, d, 1-H).

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