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Carbohydrate Research 303 (1997) 395–406

CARBOHYDRATE RESEARCH

Diastereoselective hydroboration of substituted *exo*-glucals revisited. A convenient route for the preparation of L-iduronic acid derivatives [1,2]

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Received 9 April 1997; accepted 13 May 1997

Abstract

Suitably protected derivatives of methyl 3-*O*-benzyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside, readily prepared from 3-*O*-benzyl-D-glucopyranose, were reacted with various boranes to prepare the corresponding L-idose components. Reaction of methyl 2-*O*-benzoyl-3-*O*-benzyl-6-deoxy-4-*O*-*tert*-butyldimethylsilyl-α-D-*xylo*-hex-5-enopyranoside with 9-borabicyclo[3.3.1]nonane (9-BBN) afforded an easily separable 9:1 L-*ido*:D-*gluco* mixture. The L-*ido* isomer was then transformed in a straightforward manner into suitably protected L-iduronic acid glycosyl donors (chloride, bromide, trichloroacetimidate) which could serve as highly elaborated building blocks in syntheses of L-iduronic acid containing glycosaminoglycan fragments. An unexpected side-reaction occurring in the preparation of 1-*O*-trichloroacetimidoyl derivatives is also reported. © 1997 Elsevier Science Ltd.

Keywords: Substituted *exo*-glucals; Hydroboration; L-iduronic acid; Glycosaminoglycan

1. Introduction

L-Iduronic acid is a typical component of several mammalian glycosaminoglycans, i.e. heparin, heparan sulfate and dermatan sulfate, where it plays an important role in various biological processes [1]. To study the structure-activity relationship of such polymers, there is a need for chemically pure oligosaccharide sequences which can be only prepared by chemical syntheses [2]. Any synthetic plan related to these structures should focus on an efficient preparation of this commercially non-available sugar.

Most of the preparations of this unique uronic acid, or of L-idose the parent neutral sugar, involved selective inversion of configuration at C-5 of D-*gluco* derivatives. Nucleophilic displacements of a 5-

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[1] Dedicated to Professor Hans Paulsen on the occasion of his 75th birthday.

[2] This work was presented at the XVIIIth International Carbohydrate Symposium, Milan, Italy, 1996, Abstract BP234.

PII S0008-6215(97)00149-3

sulfonate group in D-glucofuranose [3–5] or D-glucofuranuronic acid derivatives [6,7], as well as radical reduction of acetylated 5-bromouronates [8] have been reported. Another route using hydroboration of *exo*-glucal derivatives and leading to L-idose components was reported for monosaccharide [9,10] or disaccharide structures [11], but was not systematically explored.

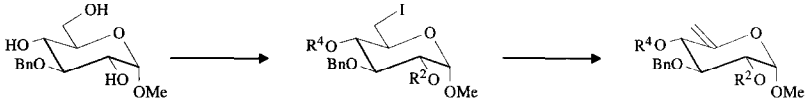
As a part of a programme devoted to the synthesis of glycosaminoglycan fragments [12], we now report on the results of a study on the diastereoselective hydroboration of variously substituted *exo*-glucal derivatives and the transformation of the L-*ido* products into L-iduronic acid components which could serve as building blocks in syntheses of L-iduronic acid containing glycosaminoglycan fragments.

2. Results and discussion

The strategies reported [5,7,13] for the syntheses of L-iduronic acid containing oligosaccharides were generally based on the use of benzyl ethers as permanent protecting groups for standing hydroxyl, and esters as semipermanent groups for the positions to be *O*-sulfonated, and the transformation D-glucose → L-idose was usually achieved at the first stage of the synthesis. For these reasons, several groups [5,14] prepared 3-*O*-benzyl-L-idopyranose from D-glucose, and used it as a starting material. Since L-iduronic acid is always α-linked, substituted at O-4, and generally 2-sulfated, and in order to avoid tedious protection reactions on L-idose derivatives, we prepared a series of suitably protected, tailor-made, *exo*-glucal components (Scheme 1) which still possess the right substituents at O-2,3 and 4. After hydroboration, the resulting L-idose derivatives could be easily transformed into L-iduronic acid synthons in few steps. Previous studies [10,15,16] showed that in hydroboration of *exo*-glucals, the formation of L-*ido* products is favoured when the substituent at C-1 (anomeric group) was located on the opposite side of the attack of the electrophile at C-5, i.e. α-oriented in the D-*gluco* series. Thus, our efforts were first directed towards the preparation of variously *O*-protected methyl α-D-*xylo*-hex-5-enopyranoside derivatives.

Treatment of known methyl 3-*O*-benzyl-α-D-glucopyranoside **1** [17] with triphenylphosphine-iodine-imidazole [18] afforded the 6-iodo derivative **2** in 86% yield. Conventional acetylation of **2** gave **3** (95%), while treatment of **2** with benzoyl chloride (1.1 equiv) in pyridine at −30 °C afforded the 2-benzoate **4** (70%).

The dehydrohalogenation of **2**–**4** was next examined. Treatment of **2** or **4** with 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) in tetrahydrofuran [19] or *N,N*-dimethylformamide at 70 °C gave only poor yields (20%) of the expected alkenes, with considerable loss of material, while treatment of **3** in *N,N*-dimethylformamide for 2.5 h afforded the *exo*-glucal **5** in 74% yield. These results contrasted with previous observations [15] where dehydrohalogenation was easily achieved on products having free hydroxyl groups. Saponification of **5** gave the crys-



1

	R^2	R^4
2	H	H
3	Ac	Ac
4	Bz	H

	R^2	R^4
5	Ac	Ac
6	H	H
7	Bz	H
8	Bz	*t*-BDMS
9	Bz	*t*-BDPS
10	Bz	ClAc
11	Piv	H
12	Piv	*t*-BDMS

Scheme 1.

talline diol **6** in 84% yield, key intermediate for the preparation of suitably protected *exo*-glucals.

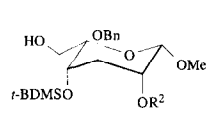
Since the semipermanent blocking group at O-2 (the position to be *O*-sulfonated) must first serve as a stereocontrolling auxiliary for the synthesis of α-L-iduronates, two routes were explored. Treatment of **6** with benzoyl chloride (1.05 equiv) or pivaloyl chloride (1.25 equiv) in pyridine at −30 °C afforded the 2-benzoate **7** and the 2-pivalate **11** in 89 and 77% yields, respectively. Various temporary protective groups were then introduced at O-4. *tert*-Butyldimethylsilylation of **7** and **11** gave **8** and **12** in 97 and 89% yields, respectively. *tert*-Butyldiphenylsilylation of **7** gave **9** (92%), whereas monochloroacetylation gave **10** (90%). The J values ($J_{1,2}$ 3.5, $J_{2,3} = J_{3,4}$ = 9.0–9.5 Hz) for the alkenes **5**–**12** suggested that all the α-glucoside compounds retained the $^4C_1$ conformation, which was not the case for β-D-analogues [20].

Having in hands a collection of *exo*-glucals, their hydroboration was next studied. The results are summarized in Table 1. As a general rule, no reaction was observed with the bulky disiamylborane [21]. For compounds **6**, **7** and **9**, solvated boranes (diborane-tetrahydrofuran or borane-methylsulfide) gave predominantly the L-*ido* products in satisfactory yields, with the exception of **9** where the sterically demanding *tert*-butyldiphenylsilyl group caused a very sluggish reaction. The 9-borabicyclo[3,3,1]nonane (9-BBN) [22] gave contrasted results, ranging from pure D-*gluco* with diol **6** to 9:1 L-*ido*:D-*gluco* ratio with the fully protected derivative **8**. In the case of **10**, extensive degradation was observed, probably because of the lability of the monochloroacetic ester, and for **12**, despite its similarly with **8**, no good selectivity could be obtained. Since satisfactory results were obtained by treatment of **8** with 9-BBN, and since in that case complete separation of the isomers could be achieved by chromatography, this reaction was carefully studied. Variations of the reaction conditions (equivalents of borane, solvent, temperature, oxidative work-up) neither changed significantly the isomeric ratio nor the overall yield. It is to be noted that the D-*gluco* isomer **14** could be recycled to **8** in 65% overall yield by iodination at C-6 (→ **15**) followed by dehydrohalogenation as reported previously.

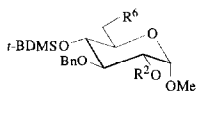
Table 1
Hydroboration of the *exo*-glucals **5**–**10** and **12** [a]

Compound	Reagent (equiv)	Oxidation [b]	Products [c]	
			ido: *gluco* ratio	Yield (%)
5	$BH_3 \cdot THF$ (2)	B	1:2.5	65
	$BH_3 \cdot Me_2S$ (2)	B	1:2	59
6	$BH_3 \cdot Me_2S$ (5)	A	4:1	80
	Sia_2BH (3.5)	A	–	–
	9-BBN (5)	A	0:100	77
7	$BH_3 \cdot THF$ (3)	B	4: 1	74
	Sia_2BH (2.5)	B	–	–
	9-BBN	B	1: 5	75
8	$BH_3 \cdot THF$ (2)	B	1:1.8	76
	$BH_3 \cdot Me_2S$ (2)	B	1:1	90
	Sia_2BH (1.5)	B	–	–
	9-BBN (2)	A	9:1 [d]	60
9	$BH_3 \cdot Me_2S$ (2)	A	4:1	44
	9-BBN (2)	A	–	–
10	9-BBN (2)	B	–	–
12	$BH_3 \cdot THF$ (2)	B	1:1	82
	9-BBN (2)	A	2:1	29

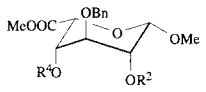
[a] All reactions were performed in dry tetrahydrofuran at 25 °C (for $BH_3 \cdot THF$ and $BH_3 \cdot Me_2S$) or at 65 °C (for Sia_2BH or 9-BBN).
[b] Oxidative work-up with 3 M NaOH (A) or phosphate buffer, pH = 7 (B).
[c] Yields and calculated ratio refer to compounds isolated after chromatography.
[d] Selected preparative conditions described in the Experimental Section.



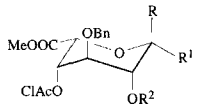
	R^2
13	Bz
16	Piv



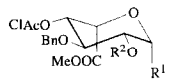
	R^2	R^6
14	Bz	OH
15	Bz	I
17	Piv	OH



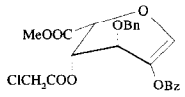
	R^2	R^4
18	Bz	*t*-BDMS
19	Bz	H
20	Bz	ClAc
21	H	*t*-BDMS
22	Piv	*t*-BDMS
23a	Piv	ClAc



	R	R^1	R^2
24	Cl	H	Bz
25	Cl	H	Piv
26	H, OH		Bz
27a	Br	H	Bz
28a	H, $OC(=NH)CCl_3$		Bz



	R^1	R^2
23b	OMe	Piv
27b	Br	Bz
28b	OBz	$C(=NH)CCl_3$



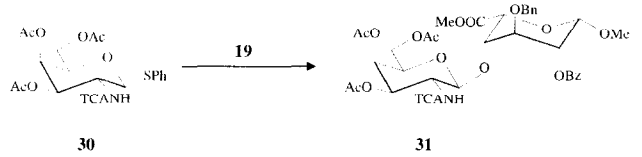
29

Several conditions for oxidizing **13** to the uronic acid derivative **18** were examined. Oxidation of **13** with pyridinium dichromate in *N,N*-dimethylformamide [23], or direct oxidation on the intermediate organoborane with chromium trioxide in aqueous acetic acid [24] gave low yields of the expected product. Treatment of **13** with catalytic ruthenium (III) chloride-sodium periodate [25], at low temperature and for a short period, led to extensive oxidation of the benzyl group at O-3 into a benzoate, though ethers of sugar derivatives were shown to be rather stable under these conditions [26]. However, the methyl uronate **18** was obtained in 79% yield by oxidation of **13** with chromium trioxide-sulfuric acid (Jones reagent) in acetone at 0 °C, followed by esterification of the intermediate acid with methyl chloroformate-4-dimethylaminopyridine in dichloromethane [27]. Attempted treatment of **18** with dichloromethyl methyl ether-zinc chloride [28] gave low yields of the expected chloride. Examination of the reaction products showed that the silyl group at O-4 was rapidly cleaved, and that the benzyl group at O-3 was affected. The temporary protecting group at O-4 was then exchanged. Treatment of **18** with tetrabutylammonium fluoride in tetrahydrofuran [29] at 0 °C furnished the alcohol **19** in 85% yield. Though **18** retained a $^1C_4$ conformation, as judged by ^{1}H NMR spectroscopy, with the labile proton at C-5 and the 4-silyloxy group in a *trans* relationship, no β-elimination reaction was observed. These results contrasted with those reported previously for methyl D-glucuronate analogues [30] where the basicity of the fluoride ion in tetrahydrofuran [31] was sufficient to cause extensive formation of unsaturated derivatives. Monochloroacetylation of **19** gave **20** in 96% yield. A similar sequence was achieved in the 2-*O*-pivaloyl series starting from the methyl uronate **18**, rather than from alcohol **16** which was not obtained easily pure through hydroboration of **12**. Transesterification of **18** with a catalytic amount of sodium methoxide in methanol at 40 °C gave the alcohol **21** in 71% yield, with small amounts of elimination products. Pivaloylation of **21** gave **22** in 96% yield, and exchange of the protecting group at O-4, as described for the preparation of **20**, gave **23** in 93% yield. The ^{1}H NMR spectrum of **23**, recorded in deuterochloroform, showed that this compound existed in solution as a ~ 1:1 mixture of two distinct conformers: **23a** under $^1C_4$ (δ 5.02, dd, $J_{1,2}$ 2.5, $J_{2,3}$ 4.0 Hz, H-2a) and **23b** under $^4C_1$ (δ 4.85, dd, $J_{1,2}$ 3.5, $J_{2,3}$ 10.0 Hz, H-2b) conformation, unlike **20** which retained exclusively the $^1C_4$ conformation.

Transformation of **20** and **23** into various glycosyl donors was achieved as follows. Treatment of **20** with dichloromethyl methyl ether-zinc chloride [28] in dichloromethane at 45 °C afforded the stable α-chloride **24** in 67% yield, whereas **23** gave **25** in only 25% yield, with extensive degradation. Both chlorides were obtained as a single anomer which retained a $^1C_4$ conformation, as judged by ^{1}H NMR. Any attempt to prepare the bromide **27a** directly, by treatment of **24** with tetrabutylammonium bromide in dry acetonitrile [32] failed, and the 2-benzoyloxyglucal **29** was isolated in 83% yield as the sole product. Chloride **24** was treated with silver oxide in aqueous acetone to afford the hemiacetal **26** in 88% yield. Treatment of **26** with (bromomethylene)dimethylammonium bromide, prepared in situ [5], gave in 65% overall yield a mixture of the bromides **27a** and **27b** which could not be separated. For L-iduronic acid derivatives, examination of the *J* values allows to estimate the preferred conformation in solution [33]. Examination of the ^{1}H NMR spectrum of the mixture

of bromides **27a** and **27b** showed that if the α-anomer **27a** retained a $^1C_4$ conformation ($J_{1,2} = J_{2,3} \leq 1.0$ Hz), the β-anomer **27b** existed in an equilibrium in which the $^4C_1$ conformation was predominant ($J_{1,2}$ 4.5, $J_{2,3}$ 8.0 Hz). Treatment of **26** with trichloroacetonitrile and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) in dichloromethane at 0 °C afforded an inseparable mixture of the imidates **28a** (α- and β-anomers) and the by-product **28b** in 65 and 30% yield, respectively, as determined by integration of the anomeric protons in the ^{1}H NMR. Formation of **28b** was assumed to be caused by base-catalyzed migration of the benzoyl group from O-2 (axial) to O-1 (equatorial, thermodynamically favoured) in **26**, followed by trichloroacetimidoylation at O-2, and change of conformation from $^1C_4$ to $^4C_1$, where thermodynamic factors and the anomeric effect are satisfied. A similar sequence (chloride → hemiacetal → imidate) was achieved starting from **25** (2-*O*-pivaloyl series, not described in the Experimental Section), and led also to a mixture of imidates and migration product in a 4:1 ratio. Use of alkali carbonates as catalyst, and variations of the solvent and of the reaction temperature did not significantly modify the distribution of the products. These results contrasted with those reported for analogues of **26** bearing a 2-*O*-acetyl group by treatment with trichloroacetonitrile and DBU [34] or potassium carbonate [14], or for a similar transformation in the L-idose series [35] with a 2-*O*-pivaloyl derivative, where no formation of migration product was apparently observed.

As a preliminary to the use of the hereby prepared derivatives for the synthesis of glycosaminoglycan fragments, the alcohol **19** was tested in glycosylation reaction (Scheme 2). We recently demonstrated [12,30] that variously *O*-protected and activated 2-deoxy-2-trichloroacetamido-D-glucopyranose derivatives are powerful glycosyl donors for the stereoselective synthesis of the 1,2-*trans*-2-amino-2-deoxy-D-glucosides, especially with uronic acid derivatives having the 4-hydroxyl free. Condensation of **19** (1 equiv) with phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-1-thio-β-D-galactopyranoside **30** [36] (1.15 equiv) in the presence of *N*-iodosuccinimide and a catalytic amount of trimethylsilyl triflate [30] afforded the disaccharide **31** in 75% yield. This successful coupling reaction opens the way for the synthesis of dermatan sulfate fragments.



30 31

Scheme 2.

In conclusion, the synthetic route now reported allows access to variously protected and/or activated L-iduronic acid derivatives. Unexpected side-reactions, such as acyl migration during trichloroacetimidoylation reaction were highlighted. Nevertheless, this route, at least in the 2-*O*-benzoyl series, is efficient and well suited for the preparation of L-iduronic acid containing glycosaminoglycan fragments, which is currently under investigation, and will be reported in due course.

3. Experimental

General methods.—Melting points were determined in capillary tubes with a Büchi apparatus and are uncorrected. Optical rotations were measured at 20–25 °C with a Perkin–Elmer 141 polarimeter. ^{1}H and ^{13}C spectra were recorded with Bruker DPX-250 or AM-300 spectrometers at 250 or 300 MHz, and 63 or 75.4 MHz, respectively, with Me_4Si as internal standard. Assignments of the protons were based on homonuclear decoupling and those of carbons by means of HETCOR experiments. C.i. (ammonia)-mass spectra were recorded with a Nermag R 10–10 spectrometer. The purity of the products was determined by TLC on Silica Gel F_{254} (E. Merck), with detection by charring with H_2SO_4. Flash-column chromatography was performed on Silica Gel (E. Merck, 40–63 μm). Elemental analyses were performed by the Service Central de Microanalyse du CNRS (Vernaison, France).

Methyl 3 - O - benzyl - 6 - deoxy - 6 - iodo - α - D - glucopyranoside (**2**).—A mixture of methyl 3-*O*-benzyl-α-D-glucopyranoside **1** [17] (5.57 g, 19.6 mmol) and Ph_3P (6.14 g, 23.5 mmol) in toluene (50 mL) was refluxed, and solvent (5 mL) was slowly distilled off at atmospheric pressure. The mixture was cooled to room temperature, imidazole (4.0 g, 58.8 mmol) and I_2 (6.49 g, 25.5 mmol) were added, and the mixture was stirred for 15 min at 120 °C, then cooled, and concd. The residue was taken up in EtOAc (100 mL), washed with brine, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column of silica gel (300 g) with 5:1

toluene–acetone to give **2** (6.64 g, 86%); mp 82–83 °C (from EtOAc–heptane); $[\alpha]_D$ +86° (*c* 1, MeOH); ^{1}H NMR [$(CD_3)_2SO$]: δ 7.30 (m, 5 H, Ph), 5.40 (d, 1 H, $J_{OH,2}$ 6.8 Hz, HO-2), 5.03 (d, 1 H, $J_{OH,4}$ 7.0 Hz, HO-4), 4.76 (s, 2 H, OCH_2Ph), 4.58 (d, 1 H, $J_{1,2}$ 3,5 Hz, H-1), and 3.34 (s, 3 H, OCH_3); MS: *m/z* 412, $[M + 18]^+$. Anal. Calcd for $C_{14}H_{19}IO_5$: C, 42.66; H, 4.86. Found: C, 42.33; H, 4.92.

*Methyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-6-iodo-α-*D*-glucopyranoside* (**3**).—A soln of **2** (950 mg, 2.4 mmol) in pyridine (10 mL) and Ac_2O (5 mL) was stirred for 2 h at room temperature, then concd. The residue was eluted from a column (60 g) of silica gel with 3:2 heptane–EtOAc to give **3** (1.09 g, 95%); mp 118–120 °C (from Et_2O–hexane); $[\alpha]_D$ +63° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 5 H, Ph), 4.96 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.87 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.86 (t, 1 H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H-4), 4.64 (ABq, 2 H, OCH_2Ph), 3.97 (t, 1 H, H-3), 3.74 (m, 1 H, $J_{5,6a}$ 2.5, $J_{5,6b}$ 9.5 Hz, H-5), 3.48 (s, 3 H, OCH_3), 3.25 (dd, 1 H, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.10 (dd, 1 H, H-6b), and 2.05, 1.96 (2 s, 6 H, 2 Ac); MS: *m/z* 496, $[M + 18]^+$, 479, $[M + 1]^+$. Anal. Calcd for $C_{18}H_{23}IO_7$: C, 45.20; H, 4.85. Found: C, 45.24; H, 4.73.

*Methyl 2-*O*-benzoyl-3-*O*-benzyl-6-deoxy-6-iodo-α-*D*-glucopyranoside* (**4**).—Benzoyl chloride (77 μL, 0.66 mmol) was added dropwise at −30 °C to a soln of **2** (237 mg, 0.6 mmol) in dry pyridine (2 mL), and the mixture was stirred for 1 h at this temperature, then allowed to attain room temperature. The mixture was diluted with CH_2Cl_2 (20 mL), washed with satd aq $NaHCO_3$, with water, dried ($MgSO_4$), and concd. The residue was eluted from a column (15 g) of silica gel with 7:3 heptane–EtOAc to give syrupy **4** (207 mg, 70%); $[\alpha]_D$ +80° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.10, 7.40 (m, 10 H, aromatic H), 5.09 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.5 Hz, H-2), 5.05 (d, 1 H, H-1), 4.75 (ABq, 2 H, OCH_2Ph), 4.03 (dd, 1 H, $J_{3,4}$ 8.5 Hz, H-3), 3.59 (dd, 1 H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 10.0 Hz, H-6a), 3.53 (m, 1 H, $J_{4,5}$ 8.5, $J_{4,OH}$ 2.5 Hz, H-4), 3.47 (m, 1 H, H-5), 3.44 (s, 3 H, OCH_3), 3.34 (dd, 1 H, $J_{5,6b}$ 6.0 Hz, H-6b), and 2.31 (d, 1 H, HO-4); MS: *m/z* 516, $[M + 18]^+$. Anal. Calcd for $C_{21}H_{23}IO_6$: C, 50.61; H, 4.63. Found: C, 50.52; H, 4.68.

*Methyl 2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-α-*D*-xylo-hex-5-enopyranoside* (**5**).—A mixture of **3** (0.5 g, 1.05 mmol) and DBU (1.54 mL, 10.5 mmol) in dry DMF (3 mL) was stirred under Ar for 2.5 h at 75 °C, then cooled, diluted with EtOAc (30 mL), washed with brine, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (20 g) of silica gel with 7:3 heptane–EtOAc containing 0.2% of Et_3N to give amorphous **5** (271 mg, 74%); $[\alpha]_D$ +48° (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 5 H, Ph), 5.45 (m, 1 H, $J_{3,4}$ 9.5, $J_{4,6a} = J_{4,6b} = 2.0$ Hz, H-4), 4.99 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.97 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.73 (t, 1 H, $J_{6a,6b}$ 2.0 Hz, H-6a), 4.68 (ABq, 2 H, OCH_2Ph), 4.50 (t, 1 H, H-6b), 4.00 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.48 (s, 3 H, OCH_3), and 2.05, 2.04 (2 s, 6 H, 2 Ac); MS: *m/z* 368, $[M + 18]^+$. Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.71; H, 6.33. Found: C, 61.74; H, 6.09.

*Methyl 3-*O*-benzyl-6-deoxy-α-*D*-xylo-hex-5-enopyranoside* (**6**).—A soln of **5** (490 mg, 1.4 mmol) in MeOH (5 mL) was treated with methanolic NaOMe (1 M, 0.2 mL) for 1.5 h at room temperature, then concd. The residue was eluted from a column (20 g) of silica gel with 3:2 heptane–EtOAc containing 0.2% Et_3N to give **6** (313 mg, 84%); mp 121–122 °C (from hexane–EtOAc); $[\alpha]_D$ +49° (*c* 1, MeOH); ^{1}H NMR ($CDCl_3$): δ 7.34 (m, 5 H, Ph), 4.85 (ABq, 2 H, OCH_2Ph), 4.82 (m, 2 H, H-1,6a), 4.72 (m, 1 H, H-6b), 4.05 (m, 1 H, $J_{3,4}$ 9,0, $J_{4,OH}$ 4.5, $J_{4,6a} = J_{4,6b} = 2.0$ Hz, H-4), 3.79 (m, 1 H, $J_{1,2}$ 3.5, $J_{2,3} = J_{2,OH} = 9.0$ Hz, H-2), 3.58 (t, 1 H, H-3), 3.47 (s, 3 H, OCH_3), 2.48 (d, 1 H, HO-4), and 2.25 (d, 1 H, HO-2); MS: *m/z* 284, $[M + 18]^+$. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.04; H, 6.95.

*Methyl 2-*O*-benzoyl-3-*O*-benzyl-6-deoxy-α-*D*-xylo-hex-5-enopyranoside* (**7**).—A mixture of **6** (790 mg, 2.97 mmol) and activated powdered 4 Å molecular sieves (200 mg) in pyridine (8 mL) was stirred for 2 h at room temperature, then cooled to −30 °C. Benzoyl chloride (0.36 mL, 3.11 mmol) was then added dropwise, and the mixture was stirred for 30 min at −30 °C, then allowed to attain room temperature. The mixture was diluted with CH_2Cl_2 (50 mL), filtered, washed with satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (30 g) of silica gel with 7:3 heptane–EtOAc containing 0.2% of Et_3N to give **7** (980 mg, 89%); mp 70–71 °C (from Et_2O–hexane); $[\alpha]_D$ +98° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.10, 7.40 (2 m, 10 H, aromatic H), 5.18 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.5 Hz, H-2), 5.09 (d, 1 H, H-1), 4.90 (t, 1 H, $J_{4,6a} = J_{6a,6b} = 2.0$ Hz, H-6a), 4.81 (ABq, 2 H, OCH_2Ph), 4.77 (t, 1 H, $J_{4,6b}$ 2.0 Hz, H-6b), 4.21 (m, 1 H, $J_{3,4}$ 9.0, $J_{4,OH}$ 4.5 Hz, H-4), 4.01 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-3), 3.42 (s, 3 H, OCH_3), and 2.49 (d, 1 H, HO-4); MS: *m/z* 388, $[M + 18]^+$, 371, $[M + 1]^+$. Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99. Found: C, 68.32; H, 6.01.

Methyl 2-O-benzoyl-3-O-benzyl-6-deoxy-4-O-tert-butyldimethylsilyl-α-D-xylo-hex-5-enopyranoside (**8**). —(*a*) *From* **7**. A mixture of **7** (2.74 g, 7.4 mmol), *tert*-butyldimethylsilyl chloride (4.48 g, 29.6 mmol) and imidazole (4.52 g, 66.6 mmol) in dry DMF (20 mL) was stirred for 2.5 h at room temperature, then diluted with EtOAc (100 mL), washed with satd aq NH_4Cl, with water, dried ($MgSO_4$), and concd. The residue was eluted from a column (140 g) of silica gel with 10:1 heptane–EtOAc containing 0.2% of Et_3N to give **8** (3.48 g, 97%); mp 91–93 °C (from cold heptane); $[\alpha]_D$ +129° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.0, 7.35 (2 m, 5 H, aromatic H), 5.18 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.5 Hz, H-2), 5.09 (d, 1 H, H-1), 4.94 (dd, 1 H, $J_{4,6a}$ 2.0, $J_{6a,6b}$ 1.0 Hz, H-6a), 4.80 (ABq, 2 H, OCH_2Ph), 4.78 (dd, 1 H, $J_{4,6b}$ 2.0 Hz, H-6b), 4.16 (m, 1 H, $J_{3,4}$ 9,0 Hz, H-4), 3.96 (dd, 1 H, H-3), 3.42 (s, 3 H, OCH_3), 0.97 (s, 9 H, C(CH_3)$_3$), and 0.10, 0.08 (2 s, 6 H, (CH_3)$_2$Si); ^{13}C ($CDCl_3$): δ 165.92 (C=O), 155.68 (C-5), 138.16–127.40 (12 C, aromatic C), 98.0 (C-1), 79.92 (C-6), 76.51 (C-2), 75.61 (C-4), 73.54 (C-3), 72.68 (*C*H_2Ph), 55.55 (O*C*H_3), 25.87, 25.65 (*C*H_3Si, Si*C*(CH$_3$)$_3$), and 18.10 (SiC(*C*H_3)$_3$); MS: *m/z* 485, $[M + 1]^+$. Anal. Calcd for $C_{27}H_{36}O_6Si$: C, 66.91; H, 7.49. Found: C, 66.78; H, 7.44.

(*b*) *From* **15**. A soln of **15** (612 mg, 1 mmol) was treated as described for the preparation of **5**. The residue was eluted from a column (40 g) of silica gel with 10:1 heptane–EtOAc containing 0.2% of Et_3N to give **8** (324 mg, 67%); mp 91–93 °C.

Methyl 2-O-benzoyl-3-O-benzyl-6-deoxy-4-O-tert-butyldiphenylsilyl-α-D-xylo-hex-5-enopyranoside (**9**). —A mixture of **7** (200 mg, 0.54 mmol) and *tert*-butyldiphenylsilyl chloride (0.56 mL, 2.16 mmol) was treated at 40 °C as described for the preparation of **8**. The residue was eluted from a column (20 g) of silica gel with 4:1 heptane–EtOAc containing 0.2% of Et_3N to give amorphous **9** (300 mg, 92%); $[\alpha]_D$ +25° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.96, 7.50 (2 m, 20 H, aromatic H), 5.06 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.0 Hz, H-2), 4.98 (d, 1 H, H-1), 4.92 (m, 1 H, H-6a), 4.65 (m, 1 H, H-6b), 4.57 (ABq, 2 H, OCH_2Ph), 4.33 (m, 1 H, $J_{3,4}$ 9.0, $J_{4,6a} = J_{4,6b} = 2.0$ Hz, H-4), 4.06 (t, 1 H, H-3), 3.38 (s, 3 H, OCH_3), and 1.10 (s, 9 H, C(CH_3)$_3$); MS: *m/z* 626, $[M + 18]^+$. Anal. Calcd for $C_{37}H_{40}O_6Si$: C, 73.00; H, 6.62. Found: C, 72.85; H, 6.60.

Methyl 2-O-benzoyl-3-O-benzyl-4-O-chloroacetyl-6-deoxy-α-D-xylo-hex-5-enopyranoside (**10**).—Monochloroacetic anhydride (138 mg, 0.81 mmol) was added at 0 °C to a soln of **7** (200 mg, 0.54 mmol) in dry pyridine (2 mL), and the mixture was stirred for 30 min at this temperature. Ice-cold water (10 mL) was then added, and the mixture was diluted with CH_2Cl_2 (20 mL), washed with satd aq $NaHCO_3$, with water, dried ($MgSO_4$), and concd. The residue was eluted from a column (20 g) of silica gel with 7:3 heptane–EtOAc containing 0.2% of Et_3N to give amorphous **10** (210 mg, 90%); $[\alpha]_D$ +73° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.07, 7.40 (2 m, 10 H, aromatic H), 5.55 (m, 1 H, $J_{3,4}$ 9.5, $J_{4,6a} = J_{4,6b} = 2.0$ Hz, H-4), 5.24 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.5 Hz, H-2), 5.15 (d, 1 H, H-1), 4.80 (t, 1 H, $J_{6a,6b}$ 2.0 Hz, H-6a), 4.73 (ABq, 2 H, OCH_2Ph), 4.58 (t, 1 H, H-6b), 4.20 (t, 1 H, H-3), 3.85 (ABq, 2 H, COCH_2Cl), and 3.44 (s, 3 H, OCH_3); MS: *m/z* 464, $[M + 18]^+$ for ^{35}Cl. Anal. Calcd for $C_{23}H_{23}ClO_7$: C, 61.82; H, 5.19; Found: C, 61.75; H, 5.21.

Methyl 3-O-benzyl-6-deoxy-2-O-pivaloyl-α-D-xylo-hex-5-enopyranoside (**11**).—A mixture of **6** (200 mg, 0.75 mmol) and activated powdered 4 Å molecular sieves (100 mg) in dry pyridine (3 mL) was stirred for 2 h at room temperature, then cooled to 0 °C. Pivaloyl chloride (166 μL, 0.99 mmol) was then added dropwise, and the mixture was stirred for 3 h at 0 °C. The mixture was diluted with CH_2Cl_2 (30 mL), washed with satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (20 g) of silica gel with 7:3 heptane–EtOAc containing 0.2% of Et_3N to give syrupy **11** (203 mg, 77%); $[\alpha]_D$ +55° (*c* 1, MeOH); ^1H NMR ($CDCl_3$): δ 7.32 (m, 5 H, Ph), 4.97 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.88 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.85 (m, 1 H, H-6a), 4.77 (ABq, 2 H, OCH_2Ph), 4.73 (m, 1 H, H-6b), 4.12 (m, 1 H, $J_{3,4}$ 9,5, $J_{4,OH}$ 4,5, $J_{4,6a} = J_{4,6b} = 2.0$ Hz, H-4), 3.85 (t, 1 H, H-3), 3.41 (s, 3 H, OCH_3), 2.38 (d, 1 H, OH-4), and 1.24 (s, 9 H, C(CH_3)$_3$); MS: *m/z* 368, $[M + 18]^+$. Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.15; H, 7.48. Found: C, 64.90; H, 7.50.

Methyl 3-O-benzyl-6-deoxy-2-O-pivaloyl-4-O-tert-butyldimethylsilyl-α-D-xylo-hex-5-enopyranoside (**12**). —Compound **11** (172 mg, 0.49 mmol) was treated as described for the preparation of **8** to give **12** (203 mg, 89%); mp 88–90 °C (from cold heptane); $[\alpha]_D$ +75° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.30 (m, 5 H, Ph), 4.97 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.91 (m, 1 H, H-6a), 4.87 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.79 (ABq, 2 H, OCH_2Ph), 4.74 (m, 1 H, H-6b), 4.08 (m, 1 H, $J_{3,4}$ 9.5, $J_{4,6a} = J_{4,6b} = 2.0$ Hz, H-4), 3.81 (t, 1 H, H-3), 3.42 (s, 3 H, OCH_3), 1.16, 0.94 (2 s, 18 H, C(CH_3)$_3$), and 0.06, 0.02 (2 s, 6 H, (CH_3)$_2$Si); MS: *m/z* 465, $[M + 1)]^+$. Anal. Calcd for $C_{25}H_{40}O_6Si$: C, 64.62; H, 8.68. Found: C, 64.31; H 8.50.

Methyl 2-O-benzoyl-3-O-benzyl-4-O-tert-butyldimethylsilyl-β-L-idopyranoside (**13**) *and methyl 2-O-benzoyl-3-O-benzyl-4-O-tert-butyldimethylsilyl-α-D-glucopyranoside* (**14**).—A soln of 9-BBN in THF (0.5 M, 4 mL, 2 mmol) was added, under Ar, to a soln of **8** (484 mg, 1 mmol) in dry THF (5 mL), and the mixture was stirred at 65 °C for 2.5 h, then cooled to room temperature. Ethanol (1 mL) was then added dropwise to consume the excess of reagent, and the resulting mixture was treated for 2 h at room temperature with 30% H_2O_2 (1.2 mL, 10 mmol) and NaOH (3 M, 1.66 mL, 5 mmol), then poured into ice-cold water (20 mL). The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the organic layer was washed with brine, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (50 g) of silica gel with 7:3 heptane–EtOAc to give first **14** (31 mg, 6%); $[\alpha]_D$ +111° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.18, 7.40 (2 m, 10 H, aromatic H), 5.28 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 10.0 Hz, H-2), 5.21 (d, 1 H, H-1), 4.97 (ABq, 2 H, OCH_2Ph), 4.20 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 3.90–3.70 (m, 4 H, H-4,5,6a,6b), 3.57 (s, 3 H, OCH_3), 1.09 (s, 9 H, C(CH_3)$_3$), and 0.38, 0.18 (2 s, 6 H, (CH_3)$_2$Si); MS: *m/z* 503, $[M + 1]^+$. Anal. Calcd for $C_{27}H_{38}O_7Si$: C, 64.51; H, 7.62. Found: C, 64.62; H, 7.59.

Next eluted was **13** (277 mg, 54%); $[\alpha]_D$ +45° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.22, 7.50 (2 m, 10 H, aromatic H), 5.31 (dd, 1 H, $J_{1,2}$ 2.5, $J_{2,3}$ 5.5 Hz, H-2), 5.08 (d, 1 H, H-1), 4.93 (ABq, 2 H, OCH_2Ph), 4.15 (m, 3 H, H-3,4,5), 3.97 (m, 2 H, H-6a,6b), 3.70 (s, 3 H, OCH_3), 2.57 (t, 1 H, *J* 4.0 Hz, HO-6), 0.91 (s, 9 H, C(CH_3)$_3$), and 0.13, 0.01 (2 s, 6 H, (CH_3)$_2$Si); MS: *m/z* 503, $[M + 1]^+$. Anal. Calcd for $C_{27}H_{38}O_7Si$: C, 64.51; H, 7.62. Found: C, 64.45; H, 7.63.

Methyl 2-O-benzoyl-3-O-benzyl-6-deoxy-6-iodo-4-O-tert-butyldimethylsilyl-α-D-glucopyranoside (**15**).—A soln of **14** (868 mg, 1.73 mmol) was treated as described for the preparation of **2**. The residue was eluted from a column (20 g) of silica gel with 3:1 heptane–EtOAc to give **15** (1.03 g, 97%); $[\alpha]_D$ +113° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.0, 7.40 (2 m, 10 H, aromatic H), 5.12 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 10.0 Hz, H-2), 5.01 (d, 1 H, H-1), 4.78 (ABq, 2 H, OCH_2Ph), 4.0 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 8.0 Hz, H-3), 3.55 (m, 2 H, H-4,5), 3.45 (s, 3 H, OCH_3), 3.25 (m, 2 H, H-6a,6b), 0.92 (s, 9 H, C(CH_3)$_3$), and 0.14, 0.04 (2 s, 6 H, (CH_3)$_2$Si); MS: *m/z* 630, $[M + 18]^+$. Anal. Calcd for $C_{27}H_{37}IO_6Si$: C, 52.94; H, 6.09. Found: C, 52.68; H, 6.18.

Methyl 3-O-benzyl-2-O-pivaloyl-4-O-tert-butyldimethylsilyl-β-L-idopyranoside (**16**) *and methyl 3-O-benzyl-2-O-pivaloyl-4-O-tert-butyldimethylsilyl-α-D-glucopyranoside* (**17**).—A soln of diborane–THF complex (1 M, 2 mL, 1 mmol) was added, under Ar, to a soln of **12** (465 mg, 1 mmol) in dry THF (5 mL), and the mixture was stirred for 4 h at room temperature. Oxidative work-up was achieved as described for the preparation of **13**. The residue was eluted from a column (40 g) of silica gel with 3:1 heptane–EtOAc to give first **17** (195 mg, 41%); $[\alpha]_D$ +83° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.42 (m, 5 H, Ph), 5.05 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.96 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.95 (ABq, 2 H, OCH_2Ph), 4.0–3.80 (m, 5 H, H-3,4,5,6a,6b), 3.54 (s, 3 H, OCH_3), 2.57 (t, 1 H, *J* 6.0 Hz, HO-6), 1.29, 1.03 (2 s, 18 H, C(CH_3)$_3$), and 0.38, 0.18 (2 s, 6 H, (CH_3)$_2$Si); MS: *m/z* 500, $[M + 18]^+$. Anal. Calcd for $C_{25}H_{42}O_7Si$: C, 62.21; H, 8.77. Found: C, 61.84; H, 8.68.

Next eluted was **16** (195 mg, 41%); $[\alpha]_D$ +61° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.36 (m, 5 H, Ph), 4.95 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.86 (dd, 1 H, $J_{2,3}$ 8.0 Hz, H-2), 4.82 (ABq, 2 H, OCH_2Ph), 4.05 (m, 5 H, H-3,4,5), 3.98 (m, 2 H, H-6a,6b), 3.54 (s, 3 H, OCH_3), 2.83 (t, 1 H, *J* 6.5 Hz, HO-6), 1.24, 0.95 (2 s, 18 H, C(CH_3)$_3$), and 0.11, 0.04 (2 s, 6 H, (CH_3)$_2$Si); MS: *m/z* 500, $[M + 18]^+$. Anal. Calcd for $C_{25}H_{42}O_7Si$: C, 62.21; H, 8.77. Found: C, 61.92; H, 8.67.

Methyl (methyl 2-O-benzoyl-3-O-benzyl-4-O-tert-butyldimethylsilyl-β-L-idopyranosid)uronate (**18**).—A soln of chromium trioxide (1.34 g) in concd H_2SO_4 (1.15 mL) and water (2.85 mL) was added dropwise at 0 °C to a stirred soln of **13** (640 mg, 1.27 mmol) in acetone (10 mL) until TLC analysis (10:1 CH_2Cl_2–MeOH) indicated complete disappearance of the starting material. Then, 2-propanol (3 mL) was added, and the mixture was diluted with EtOAc (80 mL), wash with brine, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (60 g) of silica gel with 10:1 CH_2Cl_2–MeOH to give the corresponding acid (555 mg, 84%); ^{1}H NMR ($CHCl_3$): δ 8.36, 7.60 (2 m, 10 H, aromatic H), 5.46 (m, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 3.0, $J_{2,4}$ 1.0 Hz, H-2), 5.14 (d, 1 H, H-1), 4.98 (ABq, 2 H, OCH_2Ph), 4.74 (d, 1 H, $J_{4,5}$ 2.0 Hz, H-5), 4.37 (m, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 4.15 (t, 1 H, H-3), 3.80 (s, 3 H, OCH_3), 0.88 (s, 9 H, C(CH_3)$_3$), and 0.21, 0.18 (2 s, 6 H, (CH_3)$_2$Si); MS: *m/z* 534, $[M + 18]^+$.

A mixture of the acid (408 mg, 0.79 mmol), Et_3N (130 μL, 0.91 mmol), DMAP (8 mg, 0.08 mmol), and methyl chloroformate (64 μL, 0.87 mmol) in dry CH_2Cl_2 (4 mL) was stirred for 2 h at 0 °C. Ice-cold

water was then added, and the mixture was washed with satd aq NH_4Cl, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (20 g) of silica gel with 3:1 heptane–EtOAc to give **18** (394 mg, 94%); $[\alpha]_D$ +38° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.44, 7.70 (2 m, 10 H, aromatic H), 5.49 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 3.5 Hz, H-2), 5.15 (d, 1H, H-1), 5.10 (ABq, 2 H, OCH_2Ph), 4.84 (d, 1 H, $J_{4,5}$ 2.5 Hz, H-5), 4.34 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-4), 4.25 (t, 1 H, H-3), 4.12 (s, 3 H, $COOCH_3$), 3.90 (s, 3 H, OCH_3), 0.96 (s, 9 H, $C(CH_3)_3$), and 0.18 (s, 6 H, $(CH_3)_2Si$); ^{13}C ($CDCl_3$): δ 169.20, 166.51 (2C=O), 99.59 (C-1), 75.44, 75.36 (C-2,5), 72.67, 68.72, 67.64 (C-3,4, CH_2Ph,), 57.51 (OCH_3,), 52.07 ($COOCH_3$), 25.47 ($Si(CH_3)_2$, $SiC(CH_3)_3$), and 17.73 ($C(CH_3)_3$); MS: *m/z* 548, $[M + 18]^+$. Anal. Calcd for $C_{28}H_{38}O_8Si$: C, 63.37; H, 7.02. Found: C, 63.15; H, 7.11.

Methyl (methyl 2-O-benzoyl-3-O-benzyl-β-L-idopyranosid)uronate (**19**).—A mixture of **18** (300 mg, 0.56 mmol) and Bu_4NF (294 mg, 1.13 mmol) in dry THF (3 mL) was stirred for 40 min at 0 °C under Ar, then concd. The residue was taken up in CH_2Cl_2 (40 mL), washed with satd aq NH_4Cl, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (20 g) of silica gel with 3:2 heptane–EtOAc to give **19** (200 mg, 85%); $[\alpha]_D$ +85° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.02, 7.40 (2 m, 10 H, aromatic H), 5.28 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 5.5 Hz, H-2), 4.91 (d, 1 H, H-1), 4.77 (ABq, 2 H, OCH_2Ph), 4.60 (d, 1 H, $J_{4,5}$ 2.0 Hz, H-5), 4.08 (t, 1 H, $J_{3,4}$ 5.5 Hz, H-3), 4.04 (m, 1 H, H-4, HO-4), 3.85 (s, 3 H, $COOCH_3$), and 3.56 (s, 3 H, OCH_3); MS: *m/z* 434, $[M + 18]^+$. Anal. Calcd for $C_{22}H_{24}O_8$: C, 63.45; H, 5.81. Found: C, 63.41; H, 6.08.

Methyl (methyl 2-O-benzoyl-3-O-benzyl-4-O-chloroacetyl-β-L-idopyranosid)uronate (**20**).—Compound **19** (246 mg, 0.59 mmol) was treated as described for the preparation of **10**. The residue was eluted from a column (25 g) of silica gel with 3:2 heptane–EtOAc to give **20** (278 mg, 96%); $[\alpha]_D$ +94° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.15, 7.50 (2 m, 10 H, aromatic H), 5.32 (dd, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ 2.0 Hz, H-4), 5.30 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 3.5 Hz, H-2), 4.96 (d, 1 H, H-1), 4.86 (s, 2 H, OCH_2Ph), 4.78 (d, 1 H, H-5), 4.17 (m, 1 H, H-3), 3.86 (s, 3 H, $COOCH_3$), 3.84 (ABq, 2 H, $ClCH_2CO$), and 3.63 (s, 3 H, OCH_3); MS: *m/z* 510, $[M + 18]^+$ for ^{35}Cl. Anal. Calcd for $C_{24}H_{25}ClO_9$: C, 58.48; H, 5.11. Found: C, 58.62; H 5.36.

Methyl (methyl 3-O-benzyl-4-O-tert-butyldimethylsilyl-β-L-idopyranosid)uronate (**21**).—A soln of **18** (110 mg, 0.21 mmol) in dry MeOH (3 mL) was treated for 5 h at 40 °C with methanolic NaOMe (1 M, 0.1 mL), then cooled, neutralized with Amberlite IR-120 (H^+) resin, filtered, and concd. The residue was eluted from a column (5 g) of silica gel with 3:2 heptane–EtOAc to give **21** (62 mg, 71%); $[\alpha]_D$ +65° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.43 (m, 5 H, Ph), 4.70 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1), 4.66 (ABq, 2 H, OCH_2Ph), 4.57 (d, 1 H, $J_{4,5}$ 2.0 Hz, H-5), 4.12 (m, 2 H, H-3,4), 3.84 (s, 3 H, $COOCH_3$), 3.80 (m, 1 H, H-2), 3.67 (s, 3 H, OCH_3), 0.89 (s, 9 H, $C(CH_3)_3$), and 0.04, 0.02 (2 s, 6 H, $(CH_3)_2Si$); MS: *m/z* 444, $[M + 18]^+$. Anal. Calcd for $C_{21}H_{34}O_7Si$: C, 59.13; H, 8.03. Found: C, 59.02; H, 8.05.

Methyl (methyl 3-O-benzyl-2-O-pivaloyl-4-O-tert-butyldimethylsilyl-β-L-idopyranosid)uronate (**22**).—(*a*) *From* **21**. A mixture of **21** (200 mg, 0.47 mmol), DMAP (20 mg), and pivaloyl chloride (0.3 mL, 2.34 mmol) in dry pyridine (2 mL) was stirred for 18 h at 40 °C, then cooled, diluted with CH_2Cl_2 (30 mL), washed with satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (20 g) of silica gel with 4:1 heptane–EtOAc to give **22** (231 mg, 96%); $[\alpha]_D$ +2° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.45 (m, 5 H, Ph), 5.02 (dd, 1 H, $J_{1,2}$ 2.5, $J_{2,3}$ 4.5 Hz, H-2), 4.85 (d, 1 H, H-1), 4.84 (ABq, 2 H, OCH_2Ph), 4.45 (d, 1 H, $J_{4,5}$ 3.0 Hz, H-5), 4.06 (m, 2 H, H-3,4), 3.88 (s, 3 H, $COOCH_3$), 3.57 (s, 3 H, OCH_3), 1.32, 0.94 (2 s, 18 H, $C(CH_3)_3$), and 0.08, 0.02 (2 s, 6 H, $(CH_3)_2Si$); MS: *m/z* 528, $[M + 18]^+$. Anal. Calcd for $C_{26}H_{42}O_8Si$: C, 61.15; H, 8.30. Found: C, 61.02; H, 8.25.

(*b*) *From* **16**. Compound **16** (482 mg, 1 mmol) was oxidized and esterified as described for the preparation of **18**. The residue was eluted from a column (20 g) of silica gel with 3:1 heptane–EtOAc to give **22** (245 mg, 48%); $[\alpha]_D$ +2° (*c* 1, $CHCl_3$).

Methyl (methyl 3-O-benzyl-4-O-chloroacetyl-2-O-pivaloyl-β-L-idopyranosid)uronate (**23a**, **23b**).—Compound **22** (204 mg, 0.4 mmol) was desilylated as described for the preparation of **19**, then monochloroacetylated as described for the preparation of **20**. The residue was eluted from a column (10 g) of silica gel with 3:2 heptane–EtOAc to give **23** (174 mg, 92%): ^1H NMR ($CHCl_3$): 7.30 (m, 5 H, Ph), 5.20 (dd,, 0.5 H, $J_{3,4}$ 4.0, $J_{4,5}$ 2.5 Hz, H-4a), 5.18 (dd, 0.5 H, $J_{3,4}$ 9.0, $J_{4,5}$ 10.0 Hz, H-4b), 5.08 (d, 0.5 H, $J_{1,2}$ 3.5 Hz, H-1b), 5.02 (dd, 0.5 H, $J_{1,2}$ 2.5, $J_{2,3}$ 4.0 Hz, H-2a), 4.85 (dd, 0.5 H, $J_{2,3}$ 10.0 Hz, H-2b), 4.79 (d, 0.5 H, H-1a), 4.76 (s, 1 H, OCH_2Ph), 4.65 (ABq, 1 H, OCH_2Ph), 4.62 (d, 0.5 H, H-5a), 4.25 (d, 0.5 H, H-5b), 4.07 (m, 1 H, H-3a,3b), 3.98,

3.75 (2 ABq, 2 H, $COCH_2Cl$), 3.78, 3.74 (2 s, 3 H, $COOCH_3$), 3.51, 3.42 (2 s, 3 H, OCH_3), and 1.25, 1.22 (2 s, 9 H, $C(CH_3)_3$); MS: *m/z* 490, $[M + 18]^+$ for ^{35}Cl. Anal. Calcd for $C_{22}H_{29}ClO_9$: C, 55.87; H, 6.18. Found: C, 55.72; H, 6.12.

Methyl 2-O-benzoyl-3-O-benzyl-1-chloro-4-O-chloroacetyl-1-deoxy-α-L-idopyranosyluronate (**24**). —A mixture of **20** (236 mg, 0.66 mmol), freshly fused $ZnCl_2$ (94 mg, 0.69 mmol), and dichloromethyl methyl ether (0.83 mL, 9 mmol) was stirred for 5 h at 45 °C under Ar, then cooled, diluted with CH_2Cl_2 (50 mL), washed with satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (15 g) of silica gel with 4:1 heptane–EtOAc to give **24** (220 mg, 67%); $[\alpha]_D$ −47° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.04, 7.45 (2 m, 10 H, aromatic H), 6.28 (bs, 1H, H-1), 5.40 (m, 2 H, H-2, 4), 5.22 (d, 1 H, $J_{4,5}$ 2.0 Hz, H-5), 4.85 (ABq, 2 H, OCH_2Ph), 4.01 (t, 1 H, $J_{2,3} = J_{3,4} = 3.0$ Hz, H-3), 3.91 (ABq, 2 H, $ClCH_2CO$), and 3.82 (s, 3 H, $COOCH_3$); ^{13}C ($CDCl_3$): δ 167.26, 166.27, 164.76 (3 C=O), 88.06 (C-1), 72.53, 71.55, 68.94, 68.21, 67.31 (C-2,3,4,5,CH_2Ph), 52.89 ($COOCH_3$), and 40.21 ($ClCH_2CO$); MS: *m/z* 514, $[M + 18]^+$ for ^{35}Cl. Anal. Calcd for $C_{23}H_{22}Cl_2O_8$: C, 55.56; H, 4.46. Found: C, 55.50; H, 4.35.

Methyl 3-O-benzyl-1-chloro-4-O-chloroacetyl-1-deoxy-2-O-pivaloyl-α-L-idopyranosyluronate (**25**).—Compound **23** (150 mg, 0.3 mmol) was treated and purified as described for the preparation of **24** to give **25** (30 mg, 25%); $[\alpha]_D$ −31° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.35 (m, 5 H, Ph), 6.08 (bs, 1 H, H-1), 5.35 (dd, 1 H, $J_{3,4} = J_{4,5} = 2.0$ Hz, H-4), 5.15 (d, 1 H, H-5), 5.12 (m, 1 H, $J_{2,3}$ 2.0 Hz, H-2), 4.80 (ABq, 2 H, OCH_2Ph), 4.01 (ABq, 2 H, $COCH_2Cl$), 3.81 (m, 1 H, H-3), 3.79 (s, 3 H, $COOCH_3$), and 1.15 (s, 9 H, $C(CH_3)_3$); MS: *m/z* 494, $[M + 18]^+$ for ^{35}Cl. Anal. Calcd for $C_{21}H_{26}Cl_2O_8$: C, 52.84; H, 5.49. Found: C, 52.62; H, 5.31.

Methyl 2-O-benzoyl-3-O-benzyl-4-O-chloroacetyl-α,β-L-idopyranuronate (**26**).—A mixture of **24** (116 mg, 0.23 mmol) and Ag_2O (540 mg, 2.33 mmol) in 19:1 acetone–water (4 mL) was stirred for 4 days at room temperature with protection from light. The mixture was filtered, concd, diluted with EtOAc (20 mL), washed with brine, and water, dried ($MgSO_4$), and concd. The residue was eluted from a column (8 g) of silica gel with 3:2 heptane–EtOAc to give **26** (98 mg, 88%); ^1H NMR ($CDCl_3$): δ 8.08, 7.40 (2 m, 10H, aromatic H), 5.46 (m, 0.5 H, $J_{1,OH}$ 9.0 Hz, H-1α), 5.36 (dd, 0.5 H, $J_{3,4}$ 3.0, $J_{4,5}$ 2.5 Hz, H-4α), 5.29 (dd, 0.5 H, $J_{1,2}$ 2.0, $J_{1,OH}$ 10.0 Hz, H-1β), 5.27 (dd, 0.5 H, $J_{2,3}$ 3.0 Hz, H-2α), 5.07 (d, 0.5 H, H-5α), 4.86, 4.82 (2 s, 2 H, OCH_2Ph), 4.78 (d, 0.5 H, H-5β), 4.24 (d, 0.5 H, HO-1α), 4.15 (m, 1 H, H-3α,3β), 3.82, 3.81 (2 s, 3 H, $COOCH_3$ α and β), 3.80, 3.72 (ABq, 2H, $COCH_2Cl$ α and β), and 3.58 (d, 0.5 H, HO-1β); MS: *m/z* 496, $[M + 18]^+$ for ^{35}Cl. Anal. Calcd for $C_{23}H_{23}ClO_9$: C, 57.69; H, 4.84. Found: C, 57.51; H, 4.90.

Methyl 2-O-benzoyl-3-O-benzyl-1-bromo-4-O-chloroacetyl-1-deoxy-α, and β-L-idopyranosyluronate (**27a** *and* **27b**).—A soln of oxalyl bromide in CH_2Cl_2 (1 M, 0.98 mL) was added dropwise at 5 °C to a soln of **26** (39 mg, 81 μmol) and DMF (95 μL, 1.22 mmol) in dry CH_2Cl_2 (1 mL), and the mixture was stirred for 18 h at room temperature, then diluted with cold Et_2O (30 mL), washed with satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concd to give a crude mixture of **27a** and **27b** which could not be separated by chromatography on silica gel (28 mg, 65%); ^1H NMR ($CDCl_3$): δ 8.04, 7.40 (m, 10 H, aromatic H), 6.92 (d, 0.5 H, $J_{1,2}$ 4.5 Hz, H-1b), 6.60 (bs, 0.5 H, H-1a), 5.57 (d, 0.5 H, $J_{4,5}$ 2.5 Hz, H-5b), 5.54 (m, 0.5 H, $J_{2,3}$ 2.5, $J_{2,4}$ 1.0 Hz, H-2a), 5.44 (m, 0.5 H, $J_{3,4}$ 2.5, $J_{4,5}$ 2.0 Hz, H-4a), 5.35 (dd, 0.5 H, $J_{2,3}$ 8.0 Hz, H-2b), 5.20 (d, 0.5 H, H-5a), 5.05 (dd, 0.5 H, $J_{3,4}$ 8.0 Hz, H-4b), 4.88, 4.70 (2 ABq, 2H, OCH_2Ph a and b), 4.87 (t, 0.5 H, H-3b), 4.19 (AB, 1 H, $COCH_2Cl$), 4.03 (t, 0.5 H, H-3a), 3.94 (ABq, 1 H, $COCH_2Cl$), and 3.83 3.81 (2 s, 3 H, $COOCH_3$ a and b). Anal. Calcd for $C_{23}H_{22}BrClO_8$: C, 51.00; H, 4.09. Found: C, 50.79; H, 3.97.

Attempted conversion of **24** *into* **27**.—A mixture of **24** (25 mg, 50 μmol) and Bu_4NBr (33 mg, 0.1 mmol) in dry MeCN (1 mL) was stirred for 20 h at 60 °C, then cooled, diluted with toluene (5 mL), washed with water, dried ($MgSO_4$), and concd. The residue was eluted from a column (1 g) of silica gel with 7:3 heptane–EtOAc to give syrupy methyl 1,5-anhydro-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-chloroacetyl-L-*xylo*-hex-1-enitoluronate (**29**) (20 mg, 87%); $[\alpha]_D$ −31° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.96, 7.40 (m, 10 H, aromatic H), 6.90 (s, 1 H, H-1), 5.53 (t, 1 H, $J_{3,4} = J_{4,5} = 2.0$ Hz, H-4), 4.76 (d, 1 H, H-5), 4.75 (ABq, 2 H, OCH_2Ph), 4.16 (m, 1 H, H-3), 4.14 (ABq, 2 H, $COCH_2Cl$), and 3.87 (s, 3 H, $COOCH_3$); MS: *m/z* 478, $[M + 18]^+$ for ^{35}Cl.

O-(Methyl 2-O-benzoyl-3-O-benzyl-4-O-chloroacetyl-α,β-L-idopyranosyluronate)trichloroacetimidate and methyl 1-O-benzoyl-3-O-benzyl-4-O-chloroacetyl-2-O-trichloroacetimidoyl-β-L-idopyranosyluronate (**28a** *and* **28b**).—A mixture of **26** (76 mg, 0.16 mmol), trichloroacetonitrile (0.16 mL, 1.6 mmol),

and DBU (6 μL, 40 μmol) in dry CH_2Cl_2 (1 mL) was stirred for 5 min at 0 °C, then directly eluted from a column (6 g) of silica gel with 7:3 heptane–EtOAc containing 0.2% of Et_3N to give an inseparable mixture of **28a** and **28b** (88 mg, 95%) in a 65:30 ratio; ^{1}H NMR ($CDCl_3$): δ 8.75, 8.70, 8.50 (3 s, C=N*H*), 8.05, 7.40 (2 m, 10 H, aromatic H), 6.76 (d, $J_{1,2}$ 4.5 Hz, H-1b), 6.58 (bs, H-1aα); 6.38 (d, $J_{1,2}$ 2.0 Hz, H-1aβ), 5.75 (m, H-2aα), 5.64 (dd, $J_{2,3}$ 8.0 Hz, H-2b), 5.52 (m, H-2aβ), 5.51 (d, $J_{4,5}$ 2.5 Hz, H-5b), 5.39 (m, $J_{3,4}$ 2.5, $J_{4,5}$ 2.0 Hz, H-4aα), 5.32 (m, $J_{3,4} = J_{4,5} = 2.5$ Hz, H-4aβ), 5.15 (d, H-5aα), 5.02 (dd, $J_{3,4}$ 8.0, $J_{4,5}$ 2.5 Hz, H-4b), 4.90 (d, H-5b), 5.0–4.5 (m, OC*H*$_2$Ph, H-3b), 4.21, 4.15 (2 s, COC*H*$_2$Cl), 4.18, 4.10 (2 m, H-3aα,β), 3.90 (ABq, COC*H*$_2$Cl), and 3.80, 3.79, 3.64 (3 s, COOC*H*$_3$). Anal. Calcd for $C_{25}H_{23}Cl_4NO_9$: C, 48.17; H, 3.72; N, 2.25. Found: C, 48.04; H, 3.57; N, 2.11.

O-*(3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-*β*-*D*-galactopyranosyl)-(1 → 4)-[methyl (methyl 2-*O*-benzoyl-3-*O*-benzyl-*β*-*L*-idopyranosid)uronate]* (**31**). —A mixture of **19** (24 mg, 58 μmol), phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-2-trichloroacetamido-β-D-galactopyranoside **30** [36] (39 mg, 72 μmol), NIS (16 mg, 72 μmol), and 4 Å powdered molecular sieves (50 mg) in dry CH_2Cl_2 (1 mL) was stirred for 40 min at room temperature under Ar, then cooled to 0 °C. Trimethylsilyl triflate in dry toluene (1 M, 7 μL, 7 μmol) was added, and the mixture was stirred for 30 min at 0 °C. Et_3N (5 μL) was added, and the mixture was diluted with CH_2Cl_2 (5 mL), filtered, and concd. The residue was eluted from a column (3 g) of silica gel with 5:1 toluene–EtOAc to give **31** (36 mg, 75%); $[\alpha]_D$ +8° (*c* 1.1, $CHCl_3$); ^{1}H NMR (C_6D_6): δ 8.35, 7.20 (2 m, 10 H, aromatic H), 6.85 (d, 1 H, *J* 8.5 Hz, NH), 5.56 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 2.5 Hz, H-2), 5.37 (dd, 1 H, $J_{3,4}$ 4.0, $J_{4,5}$ 1.0 Hz, H-4′), 5.33 (dd, 1 H, $J_{2,3}$ 11.0 Hz, H-3′), 4.82 (d, 1 H, H-1), 4.72 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1′), 4.70 (s, 2 H, OC*H*$_2$Ph), 4.66 (t, 1 H, $J_{3,4}$ 2.5 Hz, H-4), 4.51 (d, 1 H, $J_{4,5}$ 2.5 Hz, H-5), 4.16 (t, 1 H, H-3), 4.12 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 11.0 Hz, H-6′a), 4.02 (m, 2 H, H-2′,5′), 3.79 (dd, 1 H, $J_{5,6b}$ 6.0 Hz, H-6′b), 3.65 (s, 3 H, COOC*H*$_3$), 3.29 (s, 3 H, OC*H*$_3$), and 1.75, 1.73, 1.44 (3 s, 9 H, Ac); ^{13}C ($CDCl_3$): δ 170.20, 170.05, 169.96, 168.91, 165.98, 161.80 (6 C=O), 137.24–127.85 (12 C, aromatic C), 101.94 (C-1′), 99.60 (C-1), 92.23 (*C*Cl$_3$), 75.49 (C-3), 74.53 (C-4), 73.31 (C-5), 73.00 (*C*H$_2$Ph), 70.77 (C-5′), 69.56 (C-3′), 67.11 (C-4′), 66.25 (C-2), 61.21 (C-6′), 57.45 (OC*H*$_3$), 53.42 (C-2′), 52.81 (COOC*H*$_3$), and 20.61, 20.48, 20.20 (3 *C*H$_3$CO); MS: *m/z* 850, $[M + 1]^+$ for ^{35}Cl. Anal. Calcd for $C_{36}H_{40}Cl_3NO_{16}$: C, 50.93; H, 4.75; N, 1.65. Found: C, 50.87; H, 4.72; N, 1.52.

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