Unsaturated Carbohydrates. Part 22.[1] Alkenes from 5-Bromohexopyranose Derivatives

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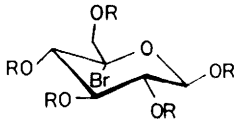
Base-catalysed elimination of hydrogen bromide from 5-bromo-β-D-glucopyranose penta-acetate and penta-benzoate gives predominantly the endocyclic products, whereas treatment with zinc–acetic acid affords a means of obtaining the exocyclic 6-deoxy-5-enose esters. All eight alkenes obtainable from these two bromo-compounds are reported together with their ^1H and ^{13}C n.m.r. spectra. Unsaturated compounds derived from penta-*O*-benzoyl-5-bromo-α-D-glucopyranose and acetylated 5-bromouronates are also reported. The conformations of all the alkenes are discussed and, in one case, the influences of the anomeric and allylic effects can be compared.

OUR general interest in carbohydrate derivatives containing double bonds [2] and, in particular, in 6-deoxyhex-5-enopyranoses from which deoxyinososes can be readily produced,[1] has led us to assess the 5-bromohexose esters described in the accompanying papers,[3,4] and related compounds, as sources of unsaturated sugars. Part of the chemical proof of the structure of penta-*O*-acetyl-5-bromo-β-D-glucopyranose (1) [3] involved its conversion with zinc–acetic acid into the known alkene (3), which is obtainable in this way from penta-*O*-acetyl-β-D-glucopyranose in *ca.* 40% yield. Formed together with the exocyclic product (3), and in smaller proportions, was the isomer (4), and in addition, one of the two possible products of dehydrobromination (5) was isolated in smaller amounts. The present report describes treatment of the



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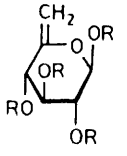
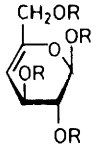
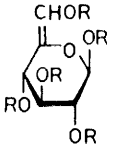
(2) R = Bz



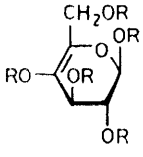
(3) R = Ac
(7) R = Bz



(4) R = Ac
(8) R = Bz



(5)
(9)



(6)
(10)

5-bromo-compound (1) with 1,5-diazabicylo[5.4.0]undec-5-ene (DBU) and the consequent production of the fourth alkene (6) as main product, and analogous elimination reactions undergone by the benzoylated analogue (2) [4] which led to the four benzoylated alkenes (7)—(10). Some alkenes produced from the α-anomer of the benzoate (2) and from methyl tetra-*O*-acetyl-5-bromo-α- and -β-D-glucopyranuronate are also reported.

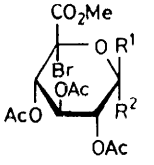
RESULTS AND DISCUSSION

While reaction of the acetylated bromide (1) with zinc–acetic acid afforded predominantly the *exo*-product (3) (*exo*: *endo* ratio *ca.* 3.5 : 1),[3] its treatment with DBU is now shown to give the crystalline endocyclic product (6) in good yield, as is consistent with *e.g.* the preferred mode of base-catalysed elimination from 1-bromo-1-methylcyclohexanes.[5] Similarly, tetra-*O*-benzoyl-α-L-sorbopyranosyl bromide gave the endocyclic product on base-catalysed elimination of hydrogen bromide.[6] However, tetra-*O*-benzyl-α,β-D-fructofuranosyl chloride which, unlike this sorbose derivative and compound (1), does not have the discrete *trans*-relationship between the hydrogen and halogen atoms undergoing elimination, gives mixed *exo*- and *endo*-cyclic products.[7] On both steric and electrostatic grounds it would be expected that the favoured rotamer state about the C-5–C-6 bond of the bromides (1) and (2) would be as depicted, and in these the bromine atoms and H-4 are suitably *anti*-orientated for *E*2 elimination. Likewise, the bromine atoms and ester groups at C-6 are similarly disposed for elimination with zinc–acetic acid, following electron donation by the metal to the bromine atoms. Otherwise, organo-zinc intermediates, formed by retention of configuration at C-5, could have decomposed by synchronous processes. Such intermediates may play a part in the Reformatsky reaction,[8] but whether they are likely to be encountered at tertiary centres as are present in the above cases is not certain. It is notable that the resonances for H-6 and H-6′ in the bromo-derivative (1) [and (2)] were well separated, whereas they coincided in the initial penta-esters, which suggests that rotation about the C-5–C-6 bond has been restricted by introduction of the bromine atom.

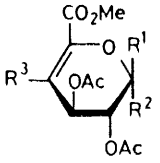
Similar results were obtained when the benzoylated bromide (2) was subjected to elimination reactions. With zinc–acetic acid it gave predominantly the exocyclic product (7) (67% isolated directly by crystallisation) with minor amounts of the alternative alkene (8) (11%, by preparative t.l.c.), and from the products of reaction with DBU, the endocyclic 4-enose ester (10) was obtained (65%, direct crystallisation). In attempts to effect substitution reactions, the bromide (2) was treated separately with sodium cyanide, sodium benzoate, and caesium fluoride in *NN*-dimethylformamide (DMF), and again gave this alkene (10) as the only detectable product rather than the compounds sought. However,

when sodium iodide in refluxing acetone or sodium thioacetate in DMF were used, the fourth alkene (9) was formed as main product, but it could be isolated only in low yield. Perhaps, in these cases, the strong nucleophiles did lead to products of substitution, which then underwent *exo*-elimination, rather than acting as bases to effect direct elimination. No saturated products were isolated.

β-Eliminations within hexopyranuronic acid derivatives afford means of obtaining 4-deoxyhex-4-enopyranuronic acid analogues and of specifically degrading hexuronic acid-containing polymers.[9] An alternative route to these unsaturated compounds was exemplified by treatment of methyl tetra-*O*-acetyl-5-bromo-β-D-glucopyranuronate (11) [10] (the yield of which was increased from 68% to 89% by use of bromine instead of *N*-bromosuccinimide for introduction of the halogen) with zinc–acetic acid which gave compound (13) in 62% yield after chromatography. Alternatively, removal of hydrogen bromide by use of DBU gave the crystalline 4-acetoxy-analogue (14) in 53% yield. When the



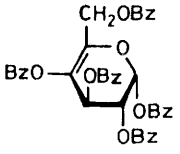
	R^1	R^2
(11)	OAc	H
(12)	H	OAc



	R^1	R^2	R^3
(13)	OAc	H	H
(14)	OAc	H	OAc
(15)	H	OAc	H

unfractionated photo-bromination products [4] derived from methyl tetra-*O*-acetyl-α-D-glucopyranuronate were treated with zinc–acetic acid the alkene (15), which has previously been obtained by base-induced elimination from a 4-*O*-sulphonylated methyl glucuronate derivative,[11] was produced in almost quantitative yield which requires that it was derived from both the 5-bromide (12) and its bromoacetyl analogue.[4] (Such debromination of bromoacetates has been noted before.[3]) Treatment of pure compound (12) with DBU did not yield a specific alkene in our hands, but the analogous alkene (16) with the β-L-*threo*-configuration, which was wanted to test a stereochemical point (see below), was readily obtained from the α-anomer [4] of the benzoylated 5-bromoglucose (2) by use of this base.

Structures of the alkenes described above were assigned largely from ^{1}H n.m.r. data (ref. 3 and Experimental section), which further indicated that all the 4-enes (4), (6), (8), (10), (13), and (14) derived from β-compounds adopted conformations close to the $^1H_2$ half-chair,[12] which is consistent with findings for related compounds.[9,13] Low $J_{1,2}$ values (*ca.* 3 Hz) were in agreement with this, as were the other significant coupling constants which could be determined from 60-MHz spectra; in particular, a $J_{3,4}$ value of 4.5 Hz for compound (13) is characteristic of three-bond allylic coupling involving a *quasi*-equatorial allylic proton.[2b] On the other hand, $J_{2,3}$ and $J_{3,4}$ values of 7 Hz and 3 Hz, respectively, for the 4-alkene (15) derived from the α-uronate indicate that it adopts a conformation akin to the $^2H_1$ alternative half-chair as shown. Therefore, in all these cases the anomeric substituent groups are axial and, except for compound (15), the allylic ester groups are *quasi*-axial, and thus they are subject to



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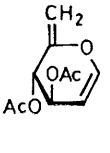
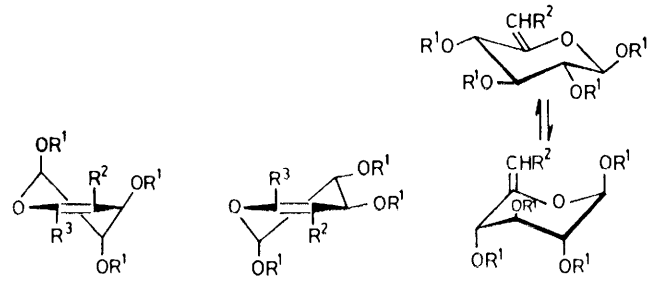


(17)

favourable anomeric [14] and allylic [15] [$A^{(1,2)}$ strain [16] effects. Compound (15) illustrates that the former of these dominates, at least in this situation, where the allylic ester group has hydrogen at the neighbouring vinylic site. To test whether this would remain so when the allylic effect was specifically enhanced by introduction of an ester group at the vinylic position concerned (C-4), 1,2,3,4,6-penta-*O*-benzoyl-β-L-*threo*-hex-4-enopyranose (16) was examined. An unchanged value for $J_{2,3}$ of 7 Hz indicates that the conformation is close to that illustrated ($^2H_1$) as the coupling constant approaches the value expected for coupling between *quasi*-axial allylic hydrogen atoms and vicinal, axial hydrogen atoms on dihydropyranyl rings in half-chair conformations.[15,17] Hence the stabilising influence of an axial ester group at C-1 still controls the conformation,



	R^1	R^2	R^3
(4)	Ac	H	CH_2OAc
(6)	Ac	OAc	CH_2OAc
(8)	Bz	H	CH_2OBz
(10)	Bz	OBz	CH_2OBz
(13)	Ac	H	CO_2Me
(14)	Ac	OAc	CO_2Me

	R^1	R^2	R^3
(15)	Ac	H	CO_2Me
(16)	Bz	OBz	CH_2OBz

	R^1	R^2
(3)	Ac	H
(5)	Ac	OAc
(7)	Bz	H
(9)	Bz	OBz

and off-sets the destabilising influence of a *quasi*-equatorial group at C-3 adjacent to another ester group on the double bond. In agreement with this, the anomeric effect for the acetoxy group is *ca.* 0.36 kJ mol^{-1},[18] whereas the allylic effect (without a substituent on the adjacent vinylic position) has been determined as being about half that value.[15,19] It would be larger in the present case, however, since a methyl group on an

adjacent vinylic position increases the value by *ca.* 0.14 kJ mol^{-1}.[19a]

In the cases of the exocyclic alkenes (3), (5), (7), and (9), $J_{1,2}$ values in the range 3—5 Hz again indicate the significance of the conformation ($^1C_4$) with all the ring ester substituent groups axial; that is, with favourable anomeric effects. In solution, tetra-*O*-acetyl- and -benzoyl-β-D-xylopyranose, which are related to these alkenes by loss of C-6, oscillate rapidly between both chair conformations,[20] the 'all axial' $^1C_4$ form representing roughly one-third and one-half of the equilibria, respectively, at room temperature ($J_{1,2}$ 6.7 and 5.1 Hz, respectively, acetone solution). In the crystal the latter adopts this state specifically,[21] while the tetra-acetate exists in a slightly distorted $^4C_1'$ chair form.[22] Introduction of the exocyclic methylene group apparently favours the $^1C_4$ conformation because the coupling constants are reduced to *ca.* 5 Hz for the acetates (3) and (5) and 3—4 Hz for the benzoates (7) and (9), suggesting that for the former the equilibria contain *ca.* 50% of each chair, and for the latter the 'all-axial' form dominates by *ca.* 3 : 1. Since introduction of a methylene group does not disturb the conformation of cyclohexane,[23] the observed effects can be ascribed to $A^{(1,3)}$ strain,[16] *i.e.* destabilising interactions between the vinylic C-6 groups and the allylic ester groups at C-4 when they are equatorial (rings in the $^4C_1$ conformation).

^{13}C Spectral data (Table) for compounds (4) and (8) showed that the C-1, C-2, and C-3 resonances were shielded relative to the corresponding resonances for penta-*O*-acetyl-[24] and -benzoyl-β-D-glucopyranose (by 3—6 p.p.m.), which is consistent with a conformational change causing the ester groups to adopt axial or *quasi*-axial orientations rather than equatorial.[25] C-6 was slightly deshielded consequent upon its having lost its equatorial character and having become allylic, but C-4 and C-5, being vinylic, were substantially deshielded and resonated near δ 98 and 150 which are similar to the chemical shifts for C-2 and C-1, respectively, observed for a series of glycal derivatives,[20] and for vinyl ethers in general.[27] Compounds (6) and (10) gave similar spectra, but C-4 was deshielded by *ca.* 29 p.p.m. by substitution of the acyloxy-groups at that position, and the other vinylic carbon atom (C-5) and C-6 were shielded by 7 and 5 p.p.m., respectively. Introduction of the 5,6-double bond to the pentaesters [compounds (3), (5), (7), and (9)] caused only small changes for the resonances for C-1—C-4 which, with minor exceptions, were shielded relative to those resonances for penta-*O*-acetyl- and -benzoyl-β-D-glucose. This is again consistent with a disturbance of the equilibria involving both chair conformations in favour of the $^1C_4$ forms. In compounds (3) and (7) C-5 and C-6 resonated as expected for vinyl ether carbon atoms, and on introduction of the acetoxy-group at C-6 in the former, C-6 was deshielded by 27 p.p.m. [compound (5)]. Such deshielding in compound (9) placed this resonance amongst those of the aromatic carbon signals and, in consequence, it was not observed. Again, the other vinyl carbon (C-5) was shielded by introduction of the ester groups at C-6, but now by 17 ± 1 p.p.m. which signifies that the mesomeric release of electrons from O-6 to C-5 approaches that observed for vinyl acetate (β-carbon atom shielded by 26 p.p.m. relative to ethylene),[27] whereas in the case of the endocyclic compounds (6) and (10) it is much less (7 p.p.m.). It appears, therefore, that mesomerism is more effective in the exocyclic cyclic situation represented by compounds (5) and (9) than in the endocyclic [(6) and (10)].

The ^{13}C n.m.r. spectrum of 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-D-*threo*-hex-1,5-dienitol (17)[3] is also included in the Table. Resonances at δ 145.4 and 149.4

^{13}C N.m.r. chemical shifts for PAG[a] and PBG[b] and unsaturated derivatives (solvent $CDCl_3$; shifts downfield from $SiMe_4$)

Compound	C-1	C-2[c]	C-3[c]	C-4[c]	C-5	C-6
PAG[a]	91.6	70.3	72.6	67.9	72.6	61.6
PBG[b]	92.8	70.9	72.9	69.2	73.2	62.7
(4)	88.4	64.3	67.3	97.4	149.6	62.3
(8)	88.4	64.3	67.6	98.4	150.0	63.2
(6)	87.9	64.2	68.5	127.0	142.2	57.8
(10)	87.9	65.1	68.9	127.4	143.1	58.7
(3)	91.5	71.0	71.7	68.1	150.0	96.5
(7)	92.2	69.8	70.9	68.5	149.7	99.5
(5)	91.1	69.6	70.5	66.5	131.6	123.7
(9)	91.9	67.4	68.5	66.4	133.8	
(16)	89.5	67.1	69.0	127.3	143.0	58.6
(17)[d]	145.4	98.3	67.5	65.0	149.4	99.1

[a] Penta-*O*-acetyl-β-D-glucopyranose; data [24] converted using δ(CS_2) = 192.8 p.p.m. [b] Penta-*O*-benzoyl-β-D-glucopyranose. [c] Except when C-4 was olefinic, these resonances were assigned using the published relative chemical shifts for these carbons of penta-*O*-acetyl-β-D-glucopyranose.[24] This procedure is not considered to be fully reliable. [d] 3,4-Di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-D-*threo*-hex-1,5-dienitol.[3]

are consistent with expectations for C-1[26] and C-5, respectively; C-2 and C-6 resonated at δ 98.3 and 99.1 as expected, and C-3 and C-4 at δ 65.0 and 67.5 [*cf.* δ 62.5 for C-3 of tri-*O*-acetyl-D-allal[26] which would be similar, and δ 68.1 for C-4 of compound (3)].

EXPERIMENTAL

Hydrogen-1 and ^{13}C n.m.r. spectra and optical rotations were measured as described in the preceding paper.

The three acetylated alkenes (3)—(5) derived from penta-*O*-acetyl-5-bromo-β-D-glucopyranose (1) by zinc–acetic acid treatment are described together with their ^{1}H n.m.r. spectra in the accompanying paper.[3]

1,2,3,4,6-*Penta*-O-*acetyl*-α-L-threo-*hex*-4-*enopyranose* (6). —A solution of DBU (0.4 g) in DMF (10 ml) was slowly added with stirring to a cooled solution of penta-*O*-acetyl-5-bromo-β-D-glucopyranose (0.58 g) in the same solvent (20 ml). After heating at 50 °C for 75 min the dark brown solution was diluted with water and extracted with chloroform (3 × 25 ml). The choroform extracts were washed with dilute hydrochloric acid, water, aqueous sodium hydrogencarbonate, again with water, dried, and solvent removed to give a dark oil which was extracted with boiling light petroleum (4 × 20 ml). Evaporation of the solvent from the extracts gave a light coloured oil (0.31 g, 65%) which crystallised on trituration with ethanol. Recrystallisation (×2) from this solvent gave the *endocyclic alkene*, m.p. 99—100 °C, $[\alpha]_D$ +50° (Found: C, 49.5; H, 5.3.

$C_{16}H_{20}O_{11}$ requires C, 49.5; H, 5.2%); δ 2.08—2.16 (15 H, 5 Ac), 4.61 (2 H, s, H-6 and -6′), 5.12 (1 H, t, $J_{1,2} = J_{2,3} = 3$ Hz, H-2), 5.46 (1 H, dd, $J_{1,3}$ 1 Hz, H-3), and 6.20 (1 H, dd, H-1).

1,2,3,4-*Tetra*-O-*benzoyl*-6-*deoxy*-β-D-xylo-*hex*-5-*enopyranose* (7).—Aqueous copper(II) sulphate (0.6 g in 5 ml) and zinc dust (9 g) were added to a solution of sodium acetate (12 g) in aqueous acetic acid (60 ml, 1 : 1). A solution of penta-*O*-benzoyl-5-bromo-β-D-glucopyranose (2) (6 g) in acetone (350 ml) was then slowly added and the mixture was stirred at room temperature for 48 h. The solids and most of the organic solvents were removed and the aqueous system was extracted with chloroform (×3). The extracts were washed with water, saturated aqueous sodium hydrogencarbonate, water, and dried before removal of the solvent. The clear syrupy residue gave the crystalline *exocyclic alkene* (2.95 g, 67%) on trituration with ethanol–chloroform (10 : 1 v/v). Recrystallised (×3) from ethanol–carbon tetrachloride (20 : 1) it had m.p. 125.5—129.5 °C. A sample further purified by preparative t.l.c. had m.p. 129—131°, $[\alpha]_D$ −8° (Found: C, 69.9; H, 4.25. $C_{34}H_{26}O_9$ requires C, 70.6; H, 4.5); δ 4.88 (1 H, br s, $J_{6,6'}$ 1.5 Hz, H-6), 5.05 (1 H, br s, H-6′), 5.70 (1 H, dd, $J_{1,2}$ 3 Hz, $J_{2,3}$ 5 Hz, H-2), 5.82 (1 H, t, $J_{3,4}$ 5 Hz, H-3), 6.16 (1 H, d, H-4), 6.63 (1 H, d, H-1), and 7.2—8.2 (20 H, phenyl).

1,2,3,6-*Tetra*-O-*benzoyl*-4-*deoxy*-α-L-threo-*hex*-4-*enopyranose* (8).—Separation of the mother-liquors obtained from the crystallisation of the 6-deoxy-hex-5-enose (7) by preparative t.l.c. gave the 4-*deoxy*-4-*enose* (0.5 g, 11%) isomer as a colourless syrup, $[\alpha]_D$ −34° (Found: C, 70.6; H, 4.7%); δ 4.88 (2 H, s, H-6 and H-6′), 5.5—5.7 (3 H, m, H-2, H-3, H-4), 6.80 (1 H, d, $J_{1,2}$ 2 Hz, H-1), and 7.1—8.1 (20 H, phenyl).

1,2,3,4,6-*Penta*-O-*benzoyl*-α-L-threo-*hex*-4-*enopyranose* (10).—(a) *With* 1,5-*diazabicyclo*[5.4.0]*undec*-5-*ene* (DBU). A solution of DBU (2.2 g, 1.1 mol equiv.) in DMF (15 ml) was added over 1.5 h with stirring at 0 °C to a solution of penta-*O*-benzoyl-5-bromo-β-D-glucopyranose (2) (10 g) in the same solvent (160 ml), and the mixture was kept at 3 °C for 18 h. After removal of the solvent the residue was taken up in chloroform, washed with dilute hydrochloric acid (×2) and water, and dried. After treatment with activated charcoal, the solvent was removed and the residue on trituration with ether gave the 4-*ene* (4.7 g). A further 1.1 g of product (total, 65%) was obtained by removing the solvent from the filtrate and trituration with ether–light petroleum. Recrystallised from aqueous acetone (1 : 5) and then acetic acid and further purified by preparative t.l.c., it had m.p. 72—74 °C, $[\alpha]_D$ +29° (Found: C, 70.2; H, 4.35. $C_{41}H_{30}O_{11}$ requires C, 70.5; H, 4.3%); δ 5.02 (2 H, s, H-6 and H-6′), 5.87 (1 H, t, $J_{1,2} = J_{2,3} = 2$ Hz, H-2), 6.12 (1 H, br s, $W_{\frac{1}{2}}$ 4 Hz, H-3), 6.87 (1 H, dd, $J_{1,3}$ 1 Hz, H-1), and 7.2—8.2 (25 H, phenyl).

(b) *With sodium benzoate in DMF*. A solution of the 5-bromo-compound (2), (2.0 g) in DMF (50 ml) was stirred with sodium benzoate (1 g) at 15 °C for 36 h. Dichloromethane (20 ml) was added and the mixture was washed with water (×4) and dried before removal of the solvent to leave a syrup (1.76 g, 98%), which had identical (t.l.c. and ^{1}H n.m.r. spectral characteristics) to the authentic 4-ene.

(c) *With sodium cyanide in DMF*. The bromo-compound (2) (1.5 g) was kept with sodium cyanide (0.75 g) in DMF (30 ml) at 15 °C for 40 h, when the dark mixture was processed in the usual way and treated with activated charcoal to give a pale yellow syrup (0.37 g). Purification by preparative t.l.c. gave the 4-ene (0.2 g), as a syrup. It gave an identical ^{1}H n.m.r. spectrum to that detailed in (a) above.

(d) *With caesium fluoride in DMF*. Caesium fluoride (0.5 g) was added to a solution of the bromo-compound (2) (0.5 g) in DMF (10 ml) and the suspension was stirred at room temperature for 8 h. Processing as above gave a syrup (0.32 g, 72%) which was shown by t.l.c. and ^{1}H n.m.r. spectroscopy to be the 4-alkene.

1,2,3,4,6-*Penta*-O-*benzoyl*-β-D-xylo-*hex*-5-*enopyranose* (9).—(a) *With sodium iodide in acetone*. A solution of the 5-bromo-compound (2) (1.0 g) and sodium iodide (4.0 g) in dry acetone (20 ml) was heated under reflux for 9 h. The solids and solvent were removed and the residue was extracted with chloroform; the dark red extract was washed with aqueous sodium thiosulphate and water, dried, and solvent removed to leave a dark yellow syrup. Trituration with ethanol gave the 5-*ene* (0.1 g, 11%) which, recrystallised from ethanol–chloroform (4 : 1), had m.p. 227—228 °C, $[\alpha]_D$ +79° (Found: C, 70.6; H, 4.2. $C_{41}H_{30}O_{11}$ requires C, 70.5; H, 4.3%); δ 5.5—5.9 (3 H, m, H-2, H-3, and H-4), 6.75 (1 H, br s, $W_{\frac{1}{2}}$ 4 Hz, H-1), 7.0—8.3 (26 H, phenyl, H-6).

(b) *With sodium thioacetate in DMF*. The 5-bromo-compound (0.5 g) was kept with sodium thioacetate (0.25 g) in DMF (10 ml) at 15 °C for 24 h. Chloroform (20 ml) was added and the solution was washed with water, and aqueous sodium hydrogencarbonate solution, dried, treated with activated charcoal, filtered, and taken to dryness to give a syrup which afforded the crystalline 5-enose (0.1 g, 22%) on trituration with ethanol–chloroform. Recrystallised from this mixed solvent it had m.p. 226—228 °C and gave an identical ^{1}H n.m.r. spectrum to that detailed above.

1,2,3,4,6-*Penta*-O-*benzoyl*-β-L-threo-*hex*-4-*enopyranose* (16).—A solution of unpurified but crystalline product (0.5 g) of the photo-bromination of penta-*O*-benzoyl-α-D-glucopyranose (1.0 g) in DMF (8 ml) was stirred at 0 °C during the slow addition of DBU (0.2 g) in the same solvent (2 ml). The black solution was stirred at room temperature for 16 h, then diluted with dichloromethane (20 ml), washed with water, dilute hydrochloric acid, and water, and dried. Removal of the solvent gave a dark syrup (0.3 g) which on preparative t.l.c. gave the 4-*ene* (0.11 g, 11% from penta-*O*-benzoyl-D-glucose), $[\alpha]_D$ +177° (Found: C, 69.6; H, 4.3. $C_{41}H_{30}O_{11}$ requires C, 70.5; H, 4.3%); δ 4.90 (2 H, s, H-6 and -6′), 5.91 (1 H, dd, $J_{1,2}$ 2.5 and $J_{2,3}$ 7 Hz, H-2), 6.48 (1 H, d, H-3), 6.80 (1 H, d, H-1), and 7.1—8.2 (25 H, phenyl).

Methyl 1,2,3-*Tri*-O-*acetyl*-4-*deoxy*-α-L-threo-*hex*-4-*enopyranuronate* (13).—Methyl tetra-*O*-acetyl-5-bromo-β-D-glucopyranuronate [10] (11) (1 g) was treated with zinc–acetic acid in a similar manner to the benzoate (2), but for 5 h. The mixture was filtered, diluted with water (100 ml) and the filtrate was extracted with chloroform (3 × 20 ml). The extracts were washed as usual and the solvent was removed to leave a syrup (0.71 g). Chromatography on a column of silica gel caused some decomposition but gave the 4-*ene* (0.43 g, 62%) as a colourless syrup, $[\alpha]_D$ +18° (Found: C, 49.5; H, 4.9. $C_{13}H_{16}O_9$ requires C, 49.4; H, 5.1%); δ 2.08 (9 H, s, 3 × OAc), 3.82 (3 H, s, OMe), 5.15 (1 H, m, $J_{1,2}$ 3, $J_{2,3}$ *ca.* 2 and $J_{2,4}$ 1.5 Hz, H-2), 5.25 (1 H, m, $J_{3,1}$ 1.5 and $J_{3,4}$ 4.5 Hz, H-3), 6.26 (1 H, dd, H-4), and 6.38 (1 H, dd, H-1). A minor, less mobile product (0.1 g, 12%) gave a ^{1}H n.m.r. spectrum which indicated it was methyl tetra-*O*-acetyl-β-D-glucopyranuronate.

Methyl 1,2,3,4-*Tetra*-O-*acetyl*-α-L-threo-*hex*-4-*enopyranuronate* (14).—A solution of DBU (2.94 g, 1.1 mol equiv.)

in DMF (15 ml) was added dropwise with stirring over 2 h to a solution of methyl tetra-*O*-acetyl-5-bromo-β-D-glucopyranuronate (11) (8.0 g) in DMF (35 ml) at 0 °C, and the mixture was kept at 3 °C for 9 days. Chloroform (80 ml) was added, and the solution was washed with water (500 ml), hydrochloric acid (dilute, ×2), and water before being dried. Treatment with activated charcoal, filtration, and removal of the solvent gave a dark yellow syrup which on trituration with ethanol at 3 °C gave the crystalline 4-*enopyranuronate* (3.5 g, 53%). Recrystallised (×3) from ethanol it had m.p. 104—105 °C, $[\alpha]_D$ +29° (Found: C, 48.2; H, 4.9. $C_{15}H_{18}O_{11}$ requires, C, 48.1; H, 4.8%); δ 2.08, 2.12, 2.12, and 2.16 (12 H, 3 s, 4 × OAc), 3.80 (3 H, s, OMe), 5.14 (1 H, t, $J_{1,2} = J_{2,3} = 2.5$ Hz, H-2), 5.48 (1 H, dd, $J_{3,1}$ 1 Hz, H-3), and 6.28 (1 H, dd, H-1).

Methyl 1,2,3-*Tri-O-acetyl*-4-*deoxy*-β-L-threo-*hex*-4-*enopyranuronate* (15).—Methyl tetra-*O*-acetyl-α-D-glucopyranuronate (1.0 g) was brominated using bromine until converted to two products,[4] and the volatile materials were removed. The residual syrup was treated as above with zinc–acetic acid (18 h) to give a syrupy product (0.83 g, 98%) which was almost chromatographically pure. Preparative t.l.c. gave the 4-*ene* (0.45 g, 53%), $[\alpha]_D$ +202° (lit.,[11] +166°) (Found: C, 49.5; H, 5.2%); δ 2.05, 2.07, and 2.12 (9 H, 3 s, 3 Ac), 3.77 (3 H, s, OMe), 5.19 (1 H, dd, $J_{1,2}$ 2.5 and $J_{2,3}$ 7 Hz, H-2), 5.52 (1 H, dd, $J_{3,4}$ 3 Hz, H-3), 6.04 (1 H, d, H-4), and 6.35 (1 H, d, H-1).

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