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THE SYNTHESES OF SOME METHYL 3-*C*-ALKYL-2,3-DIDEOXY-α-D-*glycero*-HEX-2-ENOPYRANOSID-4-ULOSES

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ABSTRACT

A general synthetic route to the title compounds is outlined which involves: (*a*) the Grignard reduction of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose; (*b*) the dehydration of the derived methyl 2-*O*-acetyl-3-*C*-alkyl-4,6-*O*-benzylidene-α-D-allopyranoside, with thionyl chloride–pyridine, at 0°, to provide the methyl 2-*O*-acetyl-3-*C*-alkyl-4,6-*O*-benzylidene-3-deoxy-α-D-*erythro*-hex-3-enopyranoside; and finally (*c*) the acid-catalyzed fragmentation of the alkene to the title compounds. Synthetic routes from the title compounds to some novel branched-chain sugars and some rotenoids are proposed.

INTRODUCTION

The literature now abounds with examples of the uses of hex-3-enopyranosid-4-uloses in synthesis of unusual sugars. These hex-3-enopyranosid-4-uloses have been unbranched, or they have had simple heteroatom (OR, SR, X) substituents, on the alkenic bond. The potential for use of these compounds in synthesis of branched-chain sugars has, however, not been realized.

We have sought to synthesize hex-2-enopyranosid-4-uloses having alkyl groups at C-2 and/or C-3, and here report our syntheses of some 3-*C*-alkyl derivatives. The fact that even an allyl side-chain may be incorporated at C-3 indicates that these new compounds will be as versatile a group of synthetic intermediates leading to the branched-chain sugars as their forerunners.

RESULTS AND DISCUSSION

We have reported[1] the efficient transformation of ketone **1** into the enone **6**, *via* the intermediates **2**, **3**, **4** and **5**, and proposed[1] the generality of the processes leading to **5**.

The two pivotal features of the synthesis of **5** were the stereospecificity of the Grignard reaction, which gave only the *allo* compound **2**, and the regiospecificity of the dehydration of **3** to the alkene **4**.

The various reductions of the ketone **1** have been described by Yoshimura *et al.*[2], who confirmed the generality of the formation of *allo* compounds as the major

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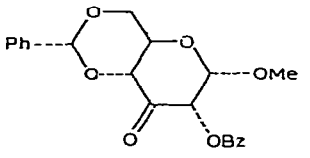

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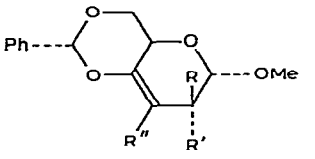
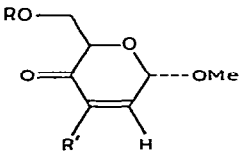
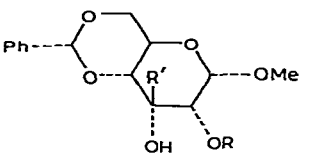


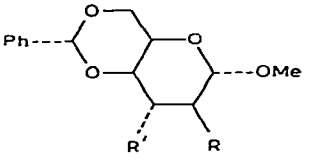
4 R = H, R′ = OAc, R″ = Me
11 R = H, R′ = OAc, R″ = CH_2Ph
15 R = H, R′ = OAc, R″ = $CH_2CH{=}CH$
19 R = Br, R′ = R″ = H
23 R = SPh, R′ = R″ = H



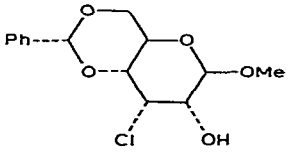
5 R = H, R′ = Me
6 R = Bz, R′ = Me
7 R = H, R′ = CH_2Ph
8 R = H, R′ = $CH_2CH{=}CH_2$
12 R = Bz, R′ = CH_2Ph
16 R = Bz, R′ = $CH_2CH{=}CH_2$
24 R = R′ = H
28 R′ = $CH_2CH{-}CH_2$ (O)



2 R = H, R′ = Me
3 R = Ac, R′ = Me
9 R = H, R′ = CH_2Ph.
10 R = Ac, R′ = CH_2Ph
13 R = H, R′ = $CH_2CH{=}CH_2$
14 R = Ac, R′ = $CH_2CH{=}CH_2$



17 R = R′ = Br
21 R = SPh, R′ = OMs



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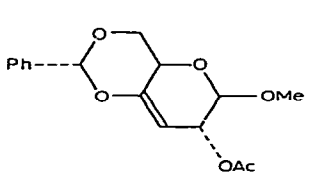
products of these reductions.

The dehydration of **3** might have been expected to yield mixtures of the three possible alkenes, by loss of the 3-hydroxyl group coupled with: (*a*) loss of the *trans*-diaxially oriented H-2; (*b*) loss of the similarly oriented H-4; or (*c*) loss of a proton from the 3-*C*-methyl group. The fact that only one product (**4**) was obtained, in 97% yield, indicated that **4** was either very much more stable than the other expected alkenes, or that H-4 was exceptionally labile. Regardless of the explanation, the marked regiospecificity of this dehydration, together with the stereospecific reduction of **1**, led us to predict that this route to **5** would be generally applicable to the syntheses of analogues of **5**.

We have now confirmed the general application of this sequence to the syntheses of analogues of **5** by realising the syntheses of **7** and **8**.



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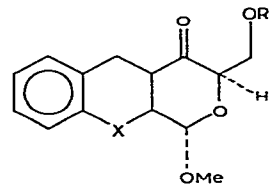

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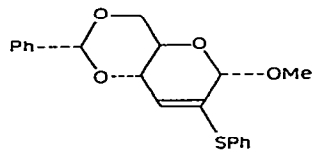

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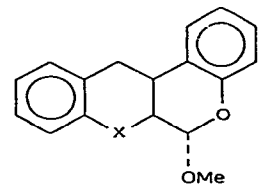

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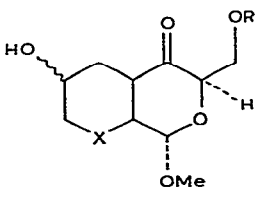

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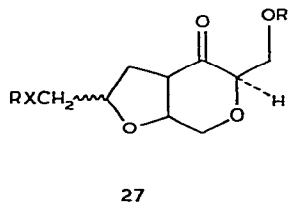

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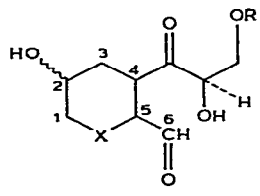

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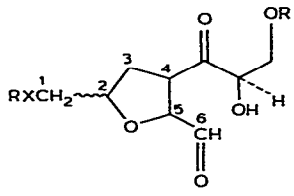
X = O, S, NR



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Reduction of **1** with benzylmagnesium bromide gave **9** in 71% yield, which was acetylated in 95% yield to provide **10**. Dehydration of **10** proceeded with the predicted regiospecificity to furnish the alkene **11** in 76% yield. This dehydration confirmed the *allo* configuration of **10**, and suggested that H-4 was indeed exceptionally labile, as one of the other possible alkenes (the styrene) must be more stable than **11**. Methanolic hydrogen chloride rapidly converted **11** into the expected compound **7** in 71% yield. Benzoylation of **7** then provided the ester **12**.

The reduction of **1** with allylmagnesium bromide provided the *allo* compound **13** in 80% yield, which was acetylated, quantitatively, to **14**. Dehydration of **14** gave **15** in 78% yield and **15** was rapidly converted into **8** by methanolic hydrogen chloride in 78% yield. Benzoylation of **8** provided the very unstable ester **16**.

Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-allopyranoside was not dehydrated by thionyl chloride–pyridine at 0° to a compound analogous to **4**. In fact, all of the methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-allopyranoside was recovered from the mixture, and we suggest that the chlorosulfite formed in the reaction was hydrolyzed during isolation. The lack of reaction of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-allopyranoside was significant, because it possesses the same stereochemical features as **3**, **10**, and **14**, namely, protons at C-2 and C-4 *trans*-diaxially oriented with respect to the 3-hydroxyl group.

The dehydration of **3**, **10**, and **14** did not, therefore, proceed by concerted elimination from the chlorosulfite intermediates, but must have arisen through tertiary carbonium-ion intermediates formed by the dissociation of the chlorosulfite. The lack of reaction of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-allopyranoside was, therefore, seen as being due to the inability of its chlorosulfite to dissociate under the conditions of the reaction, to form a secondary carbonium-ion.

Whereas the dehydration of our compounds seemed to occur without complication and in a predictable fashion, and the base-catalyzed dehydrohalogenations of compounds **17** (ref. 3) and **18** (ref. 4) also gave analogous hex-3-enopyranosides (**19** and **20**), the dehydromesylation of compound[5] **21** seemed to be less readily rationalized in yielding **22** and **23**. It must be noted that all of the compounds **19**, **20**, and **23** are potentially convertible into the simple enone **24** by our acid-catalyzed, fragmentation reaction.

Compounds **7** and **8** were well-chosen as synthetic goals, as their successful preparations prepared the way to the synthesis of heterocycles of types **25**, **26**, and **27**. Compound **25** might be generated from **1** by reduction with a suitably protected arylmagnesium halide, which on deprotection could be induced to cyclize by attacking the β-carbon atoms of the enone system. Compounds **26** and **27** might be obtained by the nucleophilic opening of an epoxide (**28**), using suitable reagents, followed by cyclization of the intermediates.

These heterocycles would offer new routes to unusual branched-chain sugars possessing chiral branches at C-4, namely, **29** and **30** from **26** and **27**, while the rotenoid skeleton **31** might be realized from **25**.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. U.v. spectra were recorded on a Varian-Cary 219 spectrophotometer and are for ethanol solutions. I.r. spectra were recorded with a Perkin–Elmer, 735B infrared spectrophotometer and are for chloroform solutions unless otherwise stated. N.m.r. spectra were recorded with a Jeol JNM-PMX60 spectrometer and are for chloroform-*d* solutions, unless otherwise stated. Chemical shifts were measured relative to tetramethylsilane as the internal standard. Specific rotations were recorded with solutions in chloroform, unless otherwise stated. Thin-layer and preparative-layer chromatography were effected on silica gel $PF_{254+366}$ (Merck), the chromatograms were observed under a Hanovia Chromatolite u.v. lamp and were made visible by exposure to iodine vapor. The petrol used as a solvent or eluant had a boiling range 60–80°. Organic solutions were dried with sodium sulfate and evaporations were performed with a rotary evaporator (Büchi) evacuated by a water pump.

Preparation of methyl 2-O-benzoyl-4,6-O-benzylidene-α-D-ribo-hexopyranosid-3-ulose (**1**). — Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (1.004 g, 2.6 mmol), in dichloromethane (20 mL) was added with stirring to Collins' reagent, prepared from chromium trioxide (1.562 g, 15.5 mmol) and pyridine (2.5 mL) in

dichloromethane (80 mL), and then acetic anhydride (1.5 mL) was immediately added to the mixture[6].

After 15 min, the excess of oxidant was decomposed by the addition of ethanol (10 mL) and the mixture filtered through a silica gel (40 g) column, with elution by ethyl acetate (200 mL). The solvent was removed to yield white crystals, of **1** (0.922 g, 92%) which were found to be pure by t.l.c. Recrystallisation from acetone–water provided needles, m.p. 209–210° (lit.[7] m.p. 211–213°), ν_{max} 1733 and 1762 cm^{-1}, δ 3.42 (s, 3 H), 5.27 and 5.57 (d, each 1 H, J 4.0 Hz, H-1 and H-2, respectively), 5.52 (s, 1 H), 7.17 (m, 8 H), and 8.17 (m, 2 H).

*Methyl 4,6-*O*-benzylidene-3-*C*-methyl-α-*D*-allopyranoside* (**2**). — A solution of **1** (7.121 g, 18.5 mmol) in benzene (800 mL) was added to an ethereal solution of methylmagnesium iodide, prepared from magnesium (10 g, 41.7 mmol), methyl iodide (34 mL) and ether (400 mL). The mixture was stirred at room temperature, under nitrogen, for 44 h, and then poured into saturated ammonium chloride (1.0 L) and the organic layer was isolated. The aqueous solution was extracted with chloroform (5 × 150 mL), and the combined organic extracts were washed with brine (2 × 200 mL), dried, and evaporated to yield a yellow gum (8.244 g) which, on trituration with ether gave white crystals of **2** (4.626 g, 84%), pure by t.l.c., m.p. 204–205° (lit.[7] m.p. 210–212°), ν_{max} 3620 cm^{-1}, δ 1.38 and 3.45 (s, each 3 H), 4.70 (m, 1 H, H-1), 5.53 (s, 1 H), and 7.33 (m, 5 H).

*Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*C*-methyl-α-*D*-allopyranoside* (**3**). — A solution of **2** (2.631 g, 8.9 mmol) in pyridine (35 mL) and acetic anhydride (35 mL) was stirred for 24 h at room temperature, and then poured onto crushed ice (600 g) and the resulting aqueous suspension extracted with chloroform (4 × 100 mL). The organic solution was washed with saturated sodium hydrogencarbonate solution (5 × 75 mL) and brine (200 mL), dried, and the solvent removed to yield a pale-yellow gum (3.145 g), pure by t.l.c., which crystallized on standing. Recrystallization from benzene–petrol provided needles of **3**, m.p. 96–97°, (lit.[2] m.p. 95–96°), ν_{max} 1740 cm^{-1}, δ 1.30, 2.17 and 3.40 (s, each 3 H), 4.70 and 4.83 (d, each 1 H, J 3.5 Hz, H-1 and H-2, respectively), 5.48 (s, 1 H), and 7.23 (m, 5 H).

*Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-*C*-methyl-α-*D*-erythro-hex-3-enopyranoside* (**4**). — To a solution of the acetate **3** (1.907 g, 5.39 mmol) in pyridine (50 mL) at 0°, thionyl chloride (0.45 mL, 5.93 mmol) was added, with stirring, and then the mixture was allowed to warm to room temperature. After 90 min, the mixture was poured into cold brine (200 mL), and the aqueous suspension extracted with ethyl acetate (4 × 100 mL). The ethyl acetate solution was washed with brine (200 mL), dried, and the solvent removed to give crystals of **4** (1.758 g, 97%), pure by t.l.c. Recrystallization from acetone–water afforded needles, m.p. 112–113°, $[\alpha]_D^{28}$ +61° (c 1.01); ν_{max} 1740 and 1720 (sh) cm^{-1}, δ 1.68 (s, 3 H, $W_{\frac{1}{2}}$ 4.0 Hz, C-CH_3), 2.10 and 3.45 (s, each 3 H, $W_{\frac{1}{2}}$ 1.0 Hz, Ac and OMe, respectively), 5.03 (d, 1 H, J 4.5, Hz, H-1), 5.43 (m, 1 H, H-2), 5.50 (s, 1 H), and 7.37 (m, 5 H).

Anal. Calc. for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.54; H, 6.27.

*Methyl 2,3-dideoxy-3-*C*-methyl-α-*D*-glycero-hex-2-enopyranosid-4-ulose* (**5**). —

Concentrated hydrochloric acid (0.5 mL) was added to a rapidly stirred solution of **4** (0.616 g, 1.9 mmol) in methanol (62 mL) at room temperature and, after 15 min, concentrated aqueous ammonia (10 mL) was added. The solvent was removed and the dried crystals triturated with hot chloroform (5 × 20 mL). Evaporation of the organic solution gave crystals of **5** (0.318 g, 96%), pure by t.l.c. and which, on recrystallization from benzene–petrol, had m.p. 98–100°, $[\alpha]_D^{28}$ +59.6° (*c*, 1.98); ν_{max} 3500 and 1688 cm^{-1}, λ_{max} 225 nm (ε 7,400); δ 1.80 (s, 3 H, $W_{\frac{1}{2}}$ 3.5 Hz, C-CH_3), 3.47 (s, 3 H, $W_{\frac{1}{2}}$ 1.5 Hz, OMe), 2.37 (m, 1 H, exchanged with D_2O), 3.93 (d, 2 H, *J* 4.0 Hz, -CH_2OH), 4.40 (t, 1 H, *J* 4.0 Hz, H-5), 5.07 (d, 1 H, *J* 4.0 Hz, H-1), and 6.57 (m, 1 H, H-2).

Anal. Calc. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.15; H, 6.87.

Methyl 3-C-benzyl-4,6-O-benzylidene-α-D-allopyranoside (**9**). — The ketone **1** (3.006 g, 7.8 mmol) in benzene (400 mL) was added to an ethereal solution of benzylmagnesium bromide, prepared from benzyl bromide (22 mL, 0.1850 mmol), magnesium (5.0 g, 0.2083 mmol), and ether (300 mL). The mixture was stirred under nitrogen for 24 h and then poured into saturated ammonium chloride solution (500 mL) and the organic layer isolated. The aqueous solution was extracted with ethyl acetate (4 × 100 mL), and the combined organic solutions were washed with brine (2 × 200 mL), dried, and then the solvent was removed to yield a yellow gum. Column chromatography, with benzene and then 2:1 petrol–acetone as eluents, yielded white crystals of **9** (2.091 g, 72%), pure by t.l.c. and which, after recrystallization from acetone–petrol, had m.p. 161–162°, $[\alpha]_D^{28}$ −28.14° (*c*, 1.02); ν_{max} 3540 cm^{-1}, δ 3.06 (s, 2 H), 3.40 (s, 3 H), 4.63 (d, 1 H, *J* 4.0 Hz, H-1), 5.42 (s, 1 H), and 7.17–7.67 (m, 10 H).

Methyl 2-O-acetyl-3-C-benzyl-4,6-O-benzylidene-α-D-allopyranoside (**10**). — A solution of **9** (0.320 g, 0.86 mmol) in pyridine (10 mL) and acetic anhydride (10 mL) was stirred for 24 h at room temperature, and then poured onto crushed ice (100 g), and the resulting aqueous suspension extracted with ethyl acetate (4 × 50 mL). The organic solution was washed with saturated sodium hydrogencarbonate solution (3 × 50 mL) and brine (100 mL), dried, and the solvent removed to yield white crystals of **10** (0.337 g, 95%) pure by t.l.c. which, on recrystallisation from chloroform–petrol, had m.p. 144–145°, $[\alpha]_D^{28}$ +5.3° (*c*l,1.0); ν_{max} 3460 and 1743 cm^{-1}; δ 2.17 and 3.35 (s, each 3 H), 3.03 (s, 2 H), 4.50 and 4.88 (d, each 1 H, *J* 4.0 Hz, H-1 and H-2, respectively), 5.40 (s, 1 H), and 6.83–7.67 (m, 10 H).

Anal. Calc. for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.06; H, 6.35.

Methyl 2-O-acetyl-3-C-benzyl-4,6-O-benzylidene-3-deoxy-α-D-erythro-hex-3-enopyranoside (**11**). — Dehydration of **10** (1.079 g, 2.6 mmol) in pyridine (20 mL) by thionyl chloride (0.24 mL, 3.31 mmol), under identical conditions as those used for the preparation of **4**, yielded a gum (1.062 g) which, on purification by p.l.c. on silica gel with 7:1 toluene–ethyl acetate as eluant, provided **11** as a gum (0.793 g, 76.5%), $[\alpha]_D^{28}$ +27.3° (*c*, 1.87); which had ν_{max} 1736 and 1706 (sh) cm^{-1}; δ 2.03 and 3.43 (s, each 3 H), 5.02 (d, 1 H, *J* 4.5 Hz, H-1), 5.43 (m, 1 H, H-2), 5.53 (s, 1 H), and 6.97–7.66 (m, 10 H).

Anal. Calc. for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.16; H, 6.17.

*Methyl 3-C-benzyl-2,3-dideoxy-α-*D-glycero-*hex-2-enopyranosid-4-ulose* (**7**). — Concentrated hydrochloric acid (1.0 mL) was added to a rapidly stirred solution of **11** (0.567 g, 1.42 mmol) in methanol (56 mL), at room temperature and, after 75 min, concentrated aqueous ammonia (15 mL) was added. The solvent was removed and the resulting semi-solid triturated with hot chloroform (5 × 25 mL). Evaporation of the chloroform gave a gum (0.372 g) which, on purification by p.l.c. on silica gel with 7:1 toluene–ethyl acetate as eluent, gave **7** as a gum (0.242 g, 71%), $[\alpha]_D^{28}$ +39.5° (*c*, 2.91); ν_{max} 3550, 3450, and 1689 cm^{-1}; λ_{max} 207 and 232 nm (ε 13,800 and 6,800); δ 2.20 (m, 1 H, exchanged with D_2O), 3.43 (s, 3 H), 3.53 (s, 2 H), 3.97 (d, 2 H, *J* 4.0 Hz, CH_2OH), 4.43 (t, 1 H, *J* 4.0 Hz, H-5), 5.07 (d, 1 H, *J* 3.5 Hz, H-1), 6.30 (m, 1 H, H-2), and 7.17 (m, 5 H).

*Methyl 6-O-benzoyl-2,3-dideoxy-3-C-benzyl-α-*D-glycero-*hex-2-enopyranosid-4-ulose* (**12**). — To a solution of **6** (0.115 g, 0.46 mmol) in pyridine (10 mL) benzoyl chloride (0.3 mL, 2.3 mmol) was added with stirring. After 24 h, the mixture was poured onto crushed ice (50 g) and the resulting aqueous solution extracted with ethyl acetate (4 × 25 mL). The organic solution was washed with saturated sodium hydrogencarbonate solution (3 × 25 mL), dried, and the solvent removed to yield a gum (0.213 g). Resolution by p.l.c. with 7:1 toluene–ethyl acetate as eluent gave **12** as a gum (0.133 g, 81%); $[\alpha]_D^{28}$ +33.2° (*c*, 1.16); ν_{max} 1720 and 1690 cm^{-1}; λ_{max} 227, 261, 269, and 278 nm (ε 18,600; 1,600; 1,400, and 1,000); δ 3.47 (s, 3 H), 3.58 (s, 2 H), 4.75 (s, 3 H, H-5 and both H-6), 5.13 (d, 1 H, *J* 4.0 Hz, H-1), 5.43 (m, 1 H, H-2), and 7.00–8.10 (m, 10 H).

*Methyl 3-C-allyl-4,6-O-benzylidene-α-*D-*allopyranoside* (**13**). — The ketone **1** (3.010 g, 7.8 mmol) dissolved in benzene (400 mL) was added to an ethereal solution of allylmagnesium bromide, prepared from allyl bromide (16 mL, 0.1849-mol), magnesium (5.0 g, 0.2083-mol), and ether (400 mL). The mixture was stirred under nitrogen for 64 h at room temperature, and then poured into saturated ammonium chloride solution (500 mL) and the organic layer isolated. The aqueous solution was extracted with ethyl acetate (4 × 100 mL) and the combined organic extracts were washed with brine (2 × 200 mL), dried, and evaporated to a gum (4.743 g). Column chromatography on silica gel (benzene) gave **13** as a gum (2.04 g, 80%) pure by t.l.c.; it was crystallized twice from chloroform–petrol to give needles, m.p. 113–114°, $[\alpha]_D^{28}$ +75.8° (*c*, 1.02); ν_{max} 3500 and 1646 cm^{-1}, δ 2.55 (d, 2 H, *J* 7.0 Hz, $-CH_2CH=CH_2$), 2.85 and 2.93 (s, each 1 H, exchanged with D_2O), 3.40 (s, 3 H), 4.72 (d, 1 H, *J* 4.0 Hz, H-1), 5.47 (s, 1 H), 4.93–6.23 (m, 3 H, $-CH=CH_2$), and 7.35 (m, 5 H).

Anal. Calc. for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.15; H, 6.87.

*Methyl 2-O-acetyl-3-C-allyl-4,6-O-benzylidene-α-*D-*allopyranoside* (**14**). — A solution of **13** (0.148 g, 0.46 mmol) in pyridine (5 mL) and acetic anhydride (5 mL) was stirred for 15 h at room temperature and then poured into crushed ice (75 g), and the resulting solution extracted with ethyl acetate (2 × 50 mL). The organic solution was washed with saturated sodium hydrogencarbonate solution (2 × 50 mL), dried, and the solvent removed to yield white crystals of **14** (0.168 g, 100%), pure by t.l.c. Recrystallization from petrol gave needles, m.p. 107–108°, $[\alpha]_D^{28}$ +55.1°

(*c*, 1.02); ν_{max} 3400, 1739 and 1637 cm^{-1}, δ 2.17 and 3.43 (s, each 3 H), 2.52 (d, 2 H, *J* 7.0 Hz), 5.52 (s, 1 H), 4.73–6.17 (5 H, H-1, H-2, $CH=CH_2$) and 7.40 (m, 5 H).

Anal. Calc. for $C_{19}H_{24}O_7$: C, 62.62; H, 6.64. Found: C, 62.42; H, 6.60.

*Methyl 2-O-acetyl-3-C-allyl-4,6-O-benzylidene-3-deoxy-α-D-*erythro*-hex-3-enopyranoside* (**15**). — To a solution of the acetate **14** (0.168 g, 0.46 mmol) in pyridine (4 mL) at 0°, thionyl chloride (0.1 mL, 1.38 mmol) was added with rapid stirring. The mixture was allowed to warm to room temperature and was stirred for a further 2.5 h. It was then poured onto crushed ice (100 g) and the resulting aqueous solution extracted with ethyl acetate (2 × 50 mL). The organic solution was washed with saturated sodium hydrogencarbonate solution (2 × 50 mL), dried, and the solvent removed to yield a gum (0.145 g). Resolution by p.l.c. with 7:1 benzene–ethyl acetate as eluent gave **15** as a gum (0.124 g, 78%); $[\alpha]_D^{28}$ +71.5° (*c*, 1.23); ν_{max} 1732, 1707 (sh) and 1642 cm^{-1}; δ 2.10 and 3.47 (s, each 3 H), 2.45–3.27 (m, 2 H, $CH_2CH=CH_2$), 5.53 (s, 1 H), 5.07 (d, 1 H, *J* 4.5 Hz, H-1), 4.83–6.40 (4 H, H-2 and $CH=CH_2$), and 7.40 (m, 5 H).

*Methyl 3-C-allyl-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranosid-4-ulose* (**8**). — Compound **15** (0.404 g, 1.17 mmol) was dissolved in methanol (40 mL) and concentrated hydrochloric acid (0.3 mL) was added to the rapidly stirred solution at room temperature. After 90 min, concentrated aqueous ammonia (10 mL) was added, and the solvents removed to give a solid, which was triturated with boiling chloroform (5 × 25 mL). Evaporation of the chloroform yielded a yellow gum (0.244 g) which on fractionation by p.l.c. with 7:1 benzene–ethyl acetate as eluent gave starting alkene (**15**) (0.019 g) and product **8** (0.172 g, 78%, based on reacted **15**). Recrystallization of **8** from petrol gave needles m.p. 73–74°, $[\alpha]_D^{28}$ +83.3° (*c*, 0.36); ν_{max} 3400, 1693 and 1649 cm^{-1}; λ_{max} 224 nm (ε 6,900); δ 2.73 (s, 1 H, exchanged with D_2O), 2.95 (d, 2 H, *J* 6.5 Hz), 3.47 (s, 3 H), 3.93 (d, 2 H, *J* 4.0 Hz, $-CH_2OH$), 4.43 (t, 1 H, *J* 4.0 Hz, H-5), 4.83–5.33 (3 H, H-1 and $CH=CH_2$), 5.40–6.17 (m, 1 H, $CH=CH_2$), and 6.57 (m, 1 H, H-2).

*Methyl 3-C-allyl-6-O-benzoyl-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranosid-4-ulose* (**16**). — The benzoate **16** was prepared from **8** by the conditions outlined previously for the benzoylation of **5** and **7**. This unstable benzoate seemed to have a half-life of ~24 h at our room temperature (~31°), and was only characterized by its i.r. and n.m.r. spectra.

Compound **16** showed ν_{max} 1640, 1697, and 1724 cm^{-1}, and signals in the n.m.r. spectrum at δ 3.00 (d, 2 H, $CH_2CH=CH_2$), 3.50 (s, 3 H), 4.73 (s, 3 H, H-5 and both H-6), 4.87–5.37 (m, 3 H, H-1 and $CH=CH_2$), 5.40–6.17 (m, 1 H, $-CH=CH_2$), 6.90 (m, 1 H, H-2), 7.37 (m, 3 H), and 7.93 (m, 2 H).

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