Branched-chain Sugars. Part 8.[1,2] The Synthesis of *C*-Acetylpyranosides and a Pillarose Derivative using 1-Methoxyvinyl-lithium

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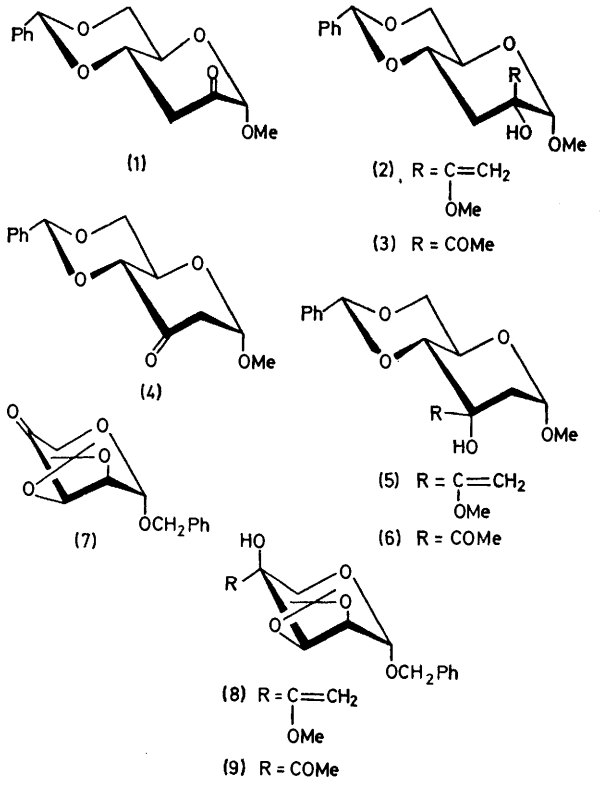
1-Methoxyvinyl-lithium, a masked acylating agent, added to the protected hexopyranosiduloses (1), (4), and (7) to give adducts that were readily hydrolysed with acid to the *C*-acetyl derivatives (3), (6), and (9), respectively. The 1-methoxyvinyl adduct (13) derived from methyl 2,3,6-trideoxy-α-L-*glycero*-hexopyranosid-4-ulose (12) gave methyl 4²-*O*-benzoyl-α-L-pillaroside (16), following oxidation with *m*-chloroperbenzoic acid in wet ether and benzoylation of the resulting 4-*C*-glycoloyl derivative (15).

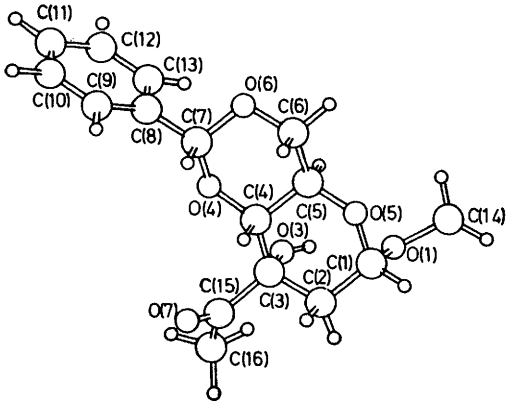
In Part 7 [1] we showed that *C*-acetyl and *C*-glycoloyl functionalities can be introduced into a protected hexofuranosulose by way of the addition of 1-methoxyvinyl-lithium,[3] a masked acylating agent. Encouraged by these results, we have also examined the reactions of 1-methoxyvinyl-lithium with a series of protected hexopyranosiduloses. This work culminated in a synthesis of methyl 4²-*O*-benzoyl-α-L-pillaroside (16).

RESULTS AND DISCUSSION

1-Methoxyvinyl-lithium [3] reacted with methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*erythro*-hexopyranosid-2-ulose [4] (1) in tetrahydrofuran–n-pentane at −60 °C to give a syrupy adduct (2) [δ($CDCl_3$): 3.60, 3 H singlet, CH_2=C*OMe*; $\nu_{max.}$ 1 625 cm^{-1} (C=C)], which was hydrolysed to



the corresponding *C*-acetyl derivative (3) with 0.02M-hydrochloric acid in aqueous 1,4-dioxan without loss of the 4,6-*O*-benzylidene group. The physical constants and ^1H n.m.r. spectrum of the 2-*C*-acetyl derivative (3) were in good agreement with those of a derivative prepared by way of the addition of metallated 2-methyl-1,3-dithian to (1) by Paulsen and his co-workers,[5] who established the D-*ribo*-configuration for their product.



Thus, 1-methoxyvinyl-lithium, like the metallated 1,3-dithian derivative,[5] adds to the carbonyl group of (1) from an axial direction, presumably so as to avoid non-bonded interactions with the α-methoxy-group.

Addition of 1-methoxyvinyl-lithium [3] to methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose [6] (4) and mild acidic hydrolysis of the resulting syrupy adduct (5) [δ($CDCl_3$): 3.66, 3 H singlet, CH_2=C*OMe*; $\nu_{max.}$ 1 625 cm^{-1} (C=C)] afforded methyl 3-*C*-acetyl-4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside (6) in an overall yield of 79%. The stereochemistry at C-3 of the 3-*C*-acetyl derivative (6) was determined by *X*-ray crystallographic analysis. A stereoview of (6) is shown in the Figure, while the final atomic co-ordinates and interatomic distances and angles are given in Tables 1 and 2 (see Experimental section), respectively. The interatomic distances and angles in (6) are unexceptional, with the pyranose and 1,3-dioxan rings adopting $^4C_1$ and $^{\alpha 4}C_{\alpha 1}$ conformations, respectively. There was no indication that 3-OH enters into intermolecular hydrogen-bonding in the crystal structure.

The reaction between 1-methoxyvinyl-lithium [3] and benzyl 2,3-*O*-isopropylidene-β-L-*erythro*-pentopyranosid-4-ulose (7) [7] afforded the syrupy adduct (8) [δ($CDCl_3$): 3.47, 3 H, singlet, CH_2=C*OMe*; $\nu_{max.}$ 1 625 cm^{-1} (C=C)], which gave benzyl 4-*C*-acetyl-2,3-*O*-isopropylidene-β-L-ribopyranoside (9) on mild acidic hydrolysis. Since

TABLE 1

Final atomic parameters for (6). E.s.d. values (in parenthesis) refer to the least significant digits

Atom	x/a	y/b	z/c
O(1)	0.1691(2)	0.3532(2)	0.4185(7)
O(3)	0.0255(2)	0.3458(2)	0.2439(5)
O(4)	−0.0675(1)	0.4461(1)	0.5593(4)
O(5)	0.1199(2)	0.4044(2)	0.7824(6)
O(6)	−0.0237(1)	0.5684(1)	0.7567(5)
O(7)	−0.0961(2)	0.2438(2)	0.6391(6)
C(1)	0.1400(2)	0.3307(3)	0.6438(10)
C(2)	0.0746(2)	0.2709(2)	0.6012(9)
C(3)	0.0092(2)	0.3185(2)	0.4831(6)
C(4)	−0.0083(2)	0.3944(2)	0.6507(6)
C(5)	0.0597(2)	0.4516(2)	0.6768(7)
C(6)	0.0403(2)	0.5250(3)	0.8468(9)
C(7)	−0.0840(2)	0.5112(2)	0.7298(7)
C(8)	−0.1500(2)	0.5630(2)	0.6458(7)
C(9)	−0.2122(2)	0.5682(3)	0.7874(8)
C(10)	−0.2728(3)	0.6176(3)	0.7150(8)
C(11)	−0.2707(2)	0.6614(3)	0.5025(8)
C(12)	−0.2079(2)	0.6566(3)	0.3581(9)
C(13)	−0.1481(2)	0.6064(3)	0.4297(7)
C(14)	0.2392(4)	0.3950(5)	0.4274(21)
C(15)	−0.0563(2)	0.2546(2)	0.4666(7)
C(16)	−0.0656(3)	0.2048(3)	0.2406(9)

TABLE 2

Interatomic distances and angles in (6)

(*a*) Distances (Å)

C(1)–O(1)	1.404(7)	C(7)–O(4)	1.415(4)
C(1)–O(5)	1.424(6)	C(7)–O(6)	1.412(4)
C(1)–C(2)	1.519(6)	C(7)–C(8)	1.511(5)
C(2)–C(3)	1.538(5)	C(8)–C(9)	1.375(5)
C(3)–O(3)	1.428(5)	C(8)–C(13)	1.378(6)
C(3)–C(4)	1.534(5)	C(9)–C(10)	1.394(6)
C(3)–C(15)	1.544(5)	C(10)–C(11)	1.364(6)
C(4)–O(4)	1.429(4)	C(11)–C(12)	1.393(6)
C(4)–C(5)	1.520(5)	C(12)–C(13)	1.389(6)
C(5)–O(5)	1.437(5)	C(14)–O(1)	1.423(8)
C(5)–C(6)	1.520(6)	C(15)–O(7)	1.211(5)
C(6)–O(6)	1.427(5)	C(15)–C(16)	1.485(6)

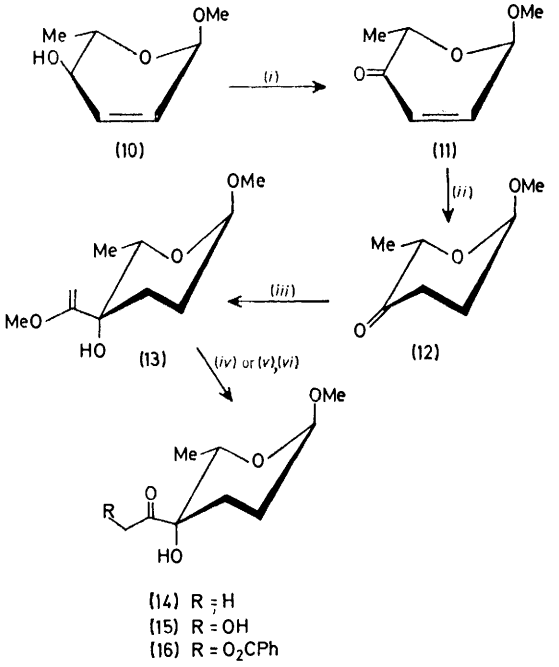
(*b*) Bond angles (°)

C(1)–O(1)–C(14)	114.5(6)	C(4)–C(5)–C(6)	108.0(3)
C(7)–O(4)–C(4)	108.5(2)	C(4)–C(5)–O(5)	110.7(3)
C(1)–O(5)–C(5)	112.2(3)	O(5)–C(5)–C(6)	107.5(3)
C(6)–O(6)–C(7)	111.4(3)	O(4)–C(7)–C(8)	109.7(3)
O(1)–C(1)–O(5)	112.4(4)	O(4)–C(7)–O(6)	110.8(3)
O(1)–C(1)–C(2)	107.6(4)	O(6)–C(7)–C(8)	107.9(3)
C(2)–C(1)–O(5)	112.0(3)	C(7)–C(8)–C(9)	119.9(3)
C(1)–C(2)–C(3)	111.8(3)	C(7)–C(8)–C(13)	120.6(3)
O(3)–C(3)–C(2)	112.5(3)	C(9)–C(8)–C(13)	119.5(3)
O(3)–C(3)–C(4)	112.5(3)	C(8)–C(19)–C(10)	120.5(4)
O(3)–C(3)–C(15)	107.0(3)	C(9)–C(10)–C(11)	120.1(4)
C(2)–C(3)–C(4)	105.3(3)	C(10)–C(11)–C(12)	119.8(4)
C(4)–C(3)–C(15)	111.7(3)	C(11)–C(12)–C(13)	119.8(4)
C(2)–C(3)–C(15)	107.8(3)	C(8)–C(13)–C(12)	120.3(4)
C(3)–C(4)–C(5)	109.8(3)	C(3)–C(15)–O(7)	119.7(3)
C(3)–C(4)–O(4)	111.5(3)	C(3)–C(15)–C(16)	118.0(3)
O(4)–C(4)–C(5)	108.1(3)	O(7)–C(15)–C(16)	122.3(4)

1-methoxyvinyl-lithium would be expected to add to the carbonyl group of (7) from the *exo*-direction with respect to the fused bicyclic ring-system, the adduct (8) is assigned the L-*ribo*-configuration.

Having established that 1-methoxyvinyl-lithium adds readily to hexopyranosiduloses, we turned our attention to the synthesis of L-pillarose. This branched-chain sugar is a component of pillaromycin A,[8] an anthracycline antibiotic produced by *Streptomyces flavovirens*. Pillaromycin A, like other members of the anthracycline group of antibiotics, displays antitumour activity, thereby accounting for the considerable interest currently shown in the synthesis of the sugar and aglycone components of these antibiotics. *X*-Ray crystallography[9] and synthetic studies[10,11] have firmly established that pillarose is 2,3,6-trideoxy-4-*C*-glycoloyl-L-*threo*-hexose rather than, as originally proposed,[12] 2,3,6-trideoxy-2-*C*-glycoloyl-L-*threo*-hexopyranos-4-ulose.

From the methodology developed in Part 7,[1] methyl α-L-pillaroside (15) should be accessible by peracid oxidation of the adduct (13) formed in the reaction between 1-methoxyvinyl-lithium and methyl 2,3,6-trideoxy-α-L-*glycero*-hexopyranosid-4-ulose (12), provided that the acylating agent adds from the equatorial direction. The keto-glycoside (12) was obtained by oxidation of methyl 2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside (10) (readily prepared[13] from L-rhamnose) with manganese dioxide[14] in chloroform, followed by selective catalytic hydrogenation of the C=C bond in the resulting enone (11). Alternatively, it could be obtained from methyl 2,3,6-trideoxy-α-L-*erythro*-hexopyranoside[13] (methyl α-L-amicetoside), the saturated analogue of (10), by oxidation with an excess of ruthenium tetraoxide[15] in carbon tetrachloride. The reaction between the keto-glycoside (12) and 1-methoxyvinyl-lithium[3] in tetrahydrofuran-n-pentane at −65 °C gave, after distillation, the crude adduct (13) in 50% yield. Mild acidic hydrolysis of the adduct (13) in aqueous 1,4-dioxan gave a single 4-*C*-acetyl derivative (14) in virtually quantitative yield, indicating that the addition of 1-methoxyvinyl-lithium, like that of other organometallic reagents,[10,11] to the keto-glycoside (12) is highly stereoselective. The stereochemistry at C-4 of the branched-chain derivatives (13) and (14) followed from the formation of methyl α-L-pillaroside (15) when the adduct (13) was oxidized



Reagents: (i) MnO_2–$CHCl_3$; (ii) H_2–Pd–C; (iii) H_2C=CHOMe–BuᵗLi; (iv) H_3O^+; (v) *m*-$ClC_6H_4CO_3H$–Et_2O–H_2O; (vi) PhCOCl–pyridine.

with a molar equivalent of *m*-chloroperbenzoic acid in wet ether. Methyl α-L-pillaroside (15) was characterised as its crystalline 4²-benzoate (16), which displayed physical and spectroscopic properties in agreement with those of the corresponding derivative of natural pillarose.[12]

EXPERIMENTAL

The experimental procedures are those used in Part 7.[1]

General Procedures for the Preparation and Hydrolysis of the Methoxyvinyl Adducts.—To a stirred solution of 1-methoxyvinyl-lithium [3] (22—30 mmol) in tetrahydrofuran–n-pentane at −60 °C under nitrogen was added dropwise the hexopyranosidulose (8 mmol) in tetrahydrofuran (40 ml), and, on complete addition, the reaction mixture was stirred at this temperature for 30 min before it was allowed to warm slowly (0.5—1 h) to 0 °C. It was then quenched with a saturated solution of ammonium chloride, the aqueous solution was extracted several times with ether, and the combined ethereal extracts were dried ($MgSO_4$) and concentrated to a syrup. Since none of the adducts was obtained in crystalline form, subsequent reactions were performed on the crude adducts, which showed a characteristic resonance at δ *ca.* 3.60 (3 H, s, CH_2=CO*Me*) in their ^{1}H n.m.r. spectra and an absorption band at $\nu_{max.}$ 1 625 cm^{-1} (C=C) in their i.r. spectra. In those instances where the i.r. spectrum of the crude product also showed an absorption band at $\nu_{max.}$ *ca.* 1 720 cm^{-1} (C=O) due to incomplete reaction of the hexopyranosidulose, the reaction was repeated using 1-methoxyvinyl-lithium (10—15 mmol).

A solution of the crude adduct (*ca.* 8 mmol) in 1,4-dioxan (100 ml) was treated with 0.04M-hydrochloric acid (100 ml) at room temperature for 3 h, and the aqueous solution was then extracted several times with chloroform. The combined chloroform extracts were washed with a saturated solution of sodium hydrogencarbonate and dried ($MgSO_4$). Removal of the solvent gave the *C*-acetyl derivative, which was purified by recrystallisation, sometimes following chromatography over silica gel [eluant methylene chloride–acetone (30 : 1)]. The i.r. spectrum of the product exhibited a characteristic absorption band at $\nu_{max.}$ *ca.* 1 710 cm^{-1} (C=O), whereas the band at $\nu_{max.}$ 1 625 cm^{-1} (C=C) in the i.r. spectrum of the adduct disappeared on hydrolysis. The yields (in parentheses) refer to the overall conversion of the hexopyranosidulose into the corresponding *C*-acetyl derivative.

Methyl 2-C-*Acetyl*-4,6-O-*benzylidene*-3-*deoxy*-α-D-ribo-*hexopyranoside* (3).—This compound (41%), m.p. 117—117.5 °C (from ether–light petroleum); $[\alpha]_D$ +108° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 420 (OH) and 1 710 cm^{-1} (C=O) (Found: C, 62.15; H, 6.7. $C_{16}H_{20}O_6$ requires C, 62.3; H, 6.5%), was prepared from methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*erythro*-hexopyranosid-2-ulose (1) [4] by the procedures described above. Its ^{1}H n.m.r. spectrum was identical to that reported for an authentic sample [lit.,[5] m.p. 117 °C, $[\alpha]_D$ +103° (*c* 1 in $CHCl_3$)].

Methyl 3-C-*Acetyl*-4,6-O-*benzylidene*-2-*deoxy*-α-D-ribo-*hexopyranoside* (6).—This compound (79%), m.p. 130—131 °C; $[\alpha]_D$ +59° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 480 (OH) and 1 715 cm^{-1} (C=O) (Found: C, 62.2; H, 6.5. $C_{16}H_{20}O_6$ requires C, 62.3; H, 6.5%), was prepared from methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose (4) [6] by the procedures described above. Its ^{1}H n.m.r. spectrum revealed salient features at δ 7.37 (5 H, m, *Ph*CH), 5.54 (1 H, s, PhC*H*), 4.86 (1 H, br d, $J_{1.2}$ 4, $J_{1,2'}$ <0.5 Hz, H-1), 3.40 (3 H, s, OMe), and 2.31 (3 H, s, COMe).

Benzyl 4-C-*Acetyl*-2,3-O-*isopropylidene*-β-L-*ribopyranoside* (9).—Application of the *C*-acylation procedure to benzyl 2,3-*O*-isopropylidene-β-L-*erythro*-pentopyranosid-4-ulose (7) (prepared [7] by oxidation of benzyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside with an excess of ruthenium tetraoxide in carbon tetrachloride) gave (9) (40%), b.p. 136 °C (bath) at 0.1 mmHg; $[\alpha]_D$ +34° (*c* 1.4 in $CHCl_3$) (Found: C, 63.6; H, 6.8. $C_{17}H_{22}O_6$ requires C, 63.3; H, 6.8%); δ 7.40 (5 H, s, *Ph*CH_2), 5.09 (1 H, br s, H-1), 4.66 (2 H, AB q, *J* 11 Hz, PhCH_2), 3.70 (2 H, AB q, *J* 12 Hz, H-5 and H-5′), 2.31 (3 H, s, COMe), and 1.59 and 1.36 (6 H, s, CMe_2).

Synthesis of Methyl 4²-O-*Benzoyl*-α-L-*pillaroside* (16). *Methyl* 2,3,6-*Trideoxy*-α-L-glycero-*hex*-2-*enopyranosid*-4-*ulose* (11).—A solution of the allylic alcohol [13] (10) (4 g) in chloroform (600 ml) containing freshly prepared manganese dioxide [14] (60 g) was stirred overnight at room temperature; t.l.c. [methylene chloride–acetone (20 : 1)] then showed that no starting material remained. Solids were filtered off and washed thoroughly with chloroform, and the combined filtrate and washings were washed with water and dried (Na_2SO_4). Removal of the solvent gave the *enone* (11) (3.4 g, 86%), m.p. 51—52 °C (after sublimation at 50 °C and *ca.* 15 mmHg); $[\alpha]_D$ −12° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 1 700 cm^{-1} (C=O) (Found: C, 58.5; H, 7.1. $C_7H_{10}O_3$ requires C, 59.1; H, 7.1%). The ^{1}H n.m.r. spectrum of (11) was identical to that reported [16] for the D-enantiomer.

Methyl 2,3,6-*Trideoxy*-α-L-glycero-*hexopyranosid*-4-*ulose* (12).—A solution of the enone (11) (3.1 g) in methanol (150 ml) containing palladium–charcoal (5%) was hydrogenated under a slight overpressure of hydrogen at room temperature until the initial adsorption of hydrogen had ceased. Removal of the catalyst and solvent, followed by chromatography on silica gel (eluant methylene chloride), furnished the *keto-glycoside* (12) (2.4 g, 76%), b.p. 80 °C (bath) at *ca.* 16 mmHg, $[\alpha]_D$ −254° (*c* 1.1 in $CHCl_3$) (Found: C, 58.3; H, 8.4. $C_7H_{12}O_3$ requires C, 58.3; H, 8.3%); δ 4.86 (1 H, t, $J_{1.2}$ and $J_{1,2'}$ 4 Hz, H-1), 4.23 (1 H, q, $J_{5,6}$ 6 Hz, H-5), 3.43 (3 H, s, OMe), 2.67—1.80 (4 H, m, CH_2–CH_2), and 1.28 (3 H, d, HC*Me*).

Alternatively, oxidation of methyl 2,3,6-trideoxy-α-L-*erythro*-hexopyranoside [13] (1 g) with ruthenium tetraoxide [15] [prepared from ruthenium dioxide dihydrate (2 g)] in carbon tetrachloride (200 ml) gave, after conventional work-up and chromatography on silica gel (eluant methylene chloride), the *keto-glycoside* (12) (0.43 g, 44%), $[\alpha]_D$ −246° (*c* 1 in $CHCl_3$), which was identical (^{1}H n.m.r. spectroscopy and t.l.c.) to the material prepared above.

Methyl 4-C-*Acetyl*-2,3,6-*trideoxy*-α-L-threo-*hexapyranoside* (14).—A solution of the keto-glycoside (12) (0.93 g, 6.45 mmol) in tetrahydrofuran (10 ml) was added dropwise to a stirred solution of 1-methoxyvinyl-lithium [3] (20 mmol) in tetrahydrofuran–n-pentane at −60 °C under nitrogen, and stirring was continued for 30 min at −60 °C. The reaction mixture was then allowed to warm to 0 °C during 30 min and it was then processed as before. Distillation of the residue gave the crude adduct (13) (0.655 g, 50%), b.p. 100—103 °C (bath) at 0.5 mmHg; $[\alpha]_D$ −92 ± 3° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 450 (OH) and 1 620 cm^{-1} (C=C); δ 3.55 and 3.37 (6 H, s, 2 × OMe). This material was contaminated with traces of other volatile products, so that satisfactory elemental analyses could not be obtained.

Hydrolysis of the adduct (13) (0.21 g) in 1,4-dioxan (17 ml) with 0.02M-hydrochloric acid (34 ml) at room temperature

for 2 h gave, after the usual work-up, the C-*acetyl derivative* (14) (0.18 g, 92%), b.p. 120 °C (bath) at 0.8 mmHg; $[\alpha]_D$ −96° (*c* 1 in $CHCl_3$); $\nu_{max.}$ 3 450 (OH) and 1 710 cm^{-1} (C=O) (Found: C, 57.5; H, 8.6. $C_9H_{16}O_4$ requires C, 57.4; H, 8.5%); δ 4.75 (1 H, d, $J_{1.2}$ 3, $J_{1.2'}$ <0.5 Hz, H-1), 4.22 (1 H, q, $J_{5,6}$ 6 Hz, H-5), 3.40 (3 H, s, OMe), 2.26 (3 H, s, COMe), and 0.98 (3 H, d, HC*Me*).

Methyl 4-C-(O-*Benzoylglycoloyl*)-2,3,6-*trideoxy*-α-L-threo-*hexopyranoside* (16).—A stirred solution of the 1-methoxyvinyl adduct (13) (0.4 g, 1.98 mmol) in wet ether (120 ml) at 0—6 °C was treated with *m*-chloroperbenzoic acid (0.35 g, 2 mmol) at room temperature for 2 h, whereafter it was washed (twice) with small volumes of sodium hydrogencarbonate solution. The aqueous washings were extracted several times with methylene chloride, and the combined organic layers were dried ($MgSO_4$) and concentrated. Chromatography of the residue (0.24 g) on silica gel [eluant methylene chloride–acetone (10 : 1)] gave methyl α-L-pillaroside (15) (0.12 g, 30%), $\nu_{max.}$ 3 400 (br, OH) and 1 710 cm^{-1} (C=O), as the last component eluted from the column.

To a solution of (15) (80 mg) in dry pyridine (0.5 ml) was added a solution of benzoyl chloride (0.1 ml) in pyridine (0.5 ml), and benzoylation was allowed to proceed overnight at room temperature. The solution was then diluted with chloroform and washed in turn with dilute hydrochloric acid and saturated solutions of sodium chloride and sodium hydrogencarbonate. Removal of the solvent from the dried ($MgSO_4$ and K_2CO_3) organic layer gave *methyl* 4²-O-*benzoyl*-α-L-*pillaroside* (16) (91 mg, 75%), m.p. 107—108 °C (from ether–n-hexane); $[\alpha]_D$ −93° (*c* 1.3 in $CHCl_3$) (Found: C, 62.0; H, 6.8. $C_{16}H_{20}O_6$ requires C, 62.3; H, 6.5%); δ 7.76 (5 H, m, *Ph*CO), 5.22 (2 H, s, H-4² and H-4²′), 4.71 (1 H, d, $J_{1.2}$ 3, $J_{1.2'}$ <0.5 Hz, H-1), 4.20 (1 H, q, $J_{5,6}$ 6 Hz, H-5), 3.35 (3 H, s, OMe), and 1.15 (3 H, d, HC*Me*). The natural L-pillaroside derivative has m.p. 103—105 °C, $[\alpha]_D$ −98.8° (*c* 0.5 in $CHCl_3$),[12] and a synthetic derivative has m.p. 104—106 °C, $[\alpha]_D$ −96° (*c* 0.5 in $CHCl_3$).[11]

Crystal Structure Determination of (6)

Crystal Data.—$C_{16}H_{20}O_6$, *M* 308.3. Orthorhombic, space group $P2_12_12_1$, a = 18.050(14), b = 15.484(15), c = 5.569(4) Å, U = 1 556.5 Å³, D_c = 1.314 g cm^{-3}, Z = 4, $F(000)$ = 656, Cu-K_α radiation, λ = 1.5418 Å, μ = 7.5 cm^{-1}.

Data Collection and Structure Analysis.—Crystals suitable for *X*-ray analysis were grown from ether–n-hexane and had m.p. 130—131 °C; they were obtained as flattened needles elongated in the *c* direction. Data were collected from three crystals mounted along the *a* (levels 0—1), *b* (levels 0—4), and *c* (levels 0—5) directions, respectively. Equi-inclination Weissenberg photographs were scanned by using a microdensitometer (S.R.C. Service, Daresbury Laboratory) and 1 203 reflections were classified as statistically significant.

The structure was solved by direct methods without difficulty. All 22 carbon and oxygen atoms appeared in the *E* map of highest figure-of-merit, and their positions and thermal parameters were refined by several rounds of full-matrix least squares. Thirteen of the strongest peaks in a weighted difference-map at *R* 0.083 could be assigned to hydrogen atoms, but the remaining hydrogen atoms could not be located. All hydrogen atoms were included at calculated positions in the last cycles of refinement in which all non-hydrogen atoms were refined anisotropically (a total of 151 variables) using a weighting scheme of the form $w = 1/(1 + 0.010F^2)$. Refinement converged to *R* 0.049.

Calculations were carried out on the University of Dundee DEC 10 computer using the SHELX 76 program.[17] Observed and calculated structure factors together with the anisotropic thermal parameters are deposited as Supplementary Publication No. SUP 22629 (9 pp.).*

The number system used (see Figure) is such that the carbon atoms of the parent hexose are numbered according to normal carbohydrate convention, while the remaining atoms are numbered arbitrarily.

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* For details see Notice to Authors No. 7, *J.C.S. Perkin I*, 1979, Index issue.

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