Reaction of 4,6-*O*-Benzylideneglycals with Benzoic Acid, Triphenylphosphine, and Diethyl Azodicarboxylate and of the Products with Sodium Methoxide. *X*-Ray Structure of 1-*O*-Benzoyl-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-α-D-*arabino*-hexopyranose, $C_{21}H_{22}O_6$

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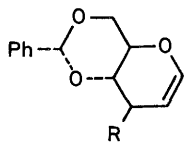
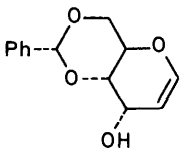
Reaction of 4,6-*O*-benzylidene-D-allal with benzoic acid, triphenylphosphine, and diethyl azodicarboxylate gave a mixture of 1-*O*-benzoyl-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranose (3) as the major product together with its β-anomer (4) and 3-*O*-benzoyl-4,6-*O*-benzylidene-D-glucal (5). Debenzoylation led to a mixture of the 4,6-*O*-benzylidene-D-glucal, 4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-D-*arabino*- and -D-*ribo*-hexopyranose. The structure of the *arabino*-isomer (6) was established by *X*-ray analysis of its 1-*O*-benzoyl derivative. Crystals are orthorhombic, space group $P2_12_12_1$, a = 21.789(2), b = 14.772(3), c = 5.925(2) Å. The structure was solved by direct methods and refined to R 0.095.

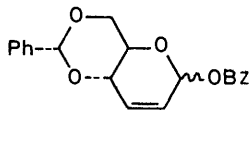
DURING studies on the reactions of the glycal (1,5-anhydro-2-deoxyhexitol) system a simple synthesis of 4,6-*O*-benzylidene-D-glucal (1) was required. This compound had previously been prepared by Sharma and Brown [1] in 30% yield by the treatment of D-glucal with



(1) R = OH



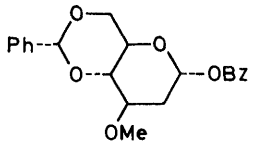
(2)



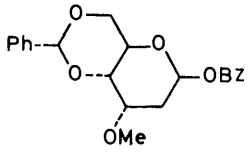
(3) α - anomer

(5) R = OBz

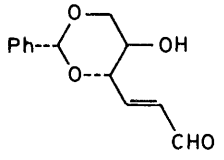
(4) β - anomer



(6)



(7)



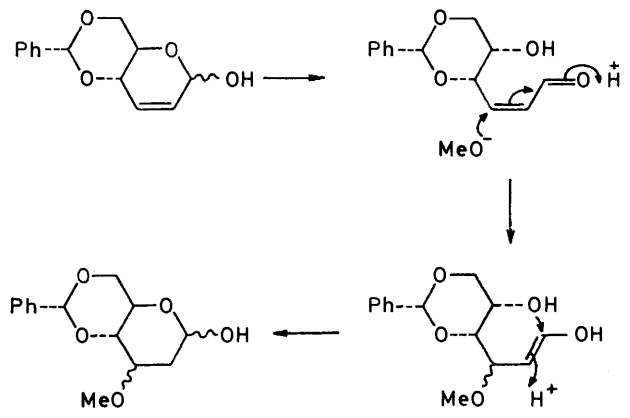
(8)

benzaldehyde and zinc chloride. However, as noted by others,[2] difficulty was experienced with this method and low yields were obtained. The C-3 epimer of (1), namely the corresponding D-allal derivative (2), is much more readily available and so inversion at C-3 in this compound provides an attractive alternative synthesis.

The reaction whereby alcohols may be converted into inverted esters by treatment with an acid, triphenylphosphine (TPP), and diethyl azodicarboxylate (DEAD) has been well described,[3,4] and has been applied to unsaturated carbohydrates by Grynkiewicz and Burzynska,[5] who reported that treatment of a series of methyl α- and β-pent-2-enopyranosides and hex-2-enopyranosides bearing a free hydroxy-group at C-4 with benzoic acid, TPP and DEAD, gave only the S_N2 products. This method appeared to provide a solution to the problem. Treatment of 4,6-*O*-benzylidene-D-allal (2) with the above reagent system afforded a mixture of three compounds, the major component of which was not the required glucal (5), but was identified as 1-*O*-benzoyl-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranose (3) on the basis of the ^1H and ^{13}C n.m.r. spectra (see Experimental section). In addition to further (3), the mother-liquors contained its anomer (4), the structure of which was assigned on the basis of the similarity of the ^1H and ^{13}C n.m.r. spectra to those of (3) and 3-*O*-benzoyl-4,6-*O*-benzylidene-D-glucal (5). The presence of (5) was confirmed by a comparison of the ^{13}C and ^1H spectra of the mother-liquors with those of a sample of (5) prepared by benzoylation of (1).

This mixture of compounds from the mother-liquors could not be resolved by chromatography. However, debenzoylation of the mother-liquor with sodium methoxide in methanol followed by chromatography afforded 6-*O*-benzylidene-D-glucal (1), and an unresolved mixture of two other compounds. Re-benzoylation of these two compounds followed by chromatography afforded two crystalline benzoates of which the ^1H and ^{13}C n.m.r. spectra indicated that both were saturated 2-deoxy-sugars containing a methoxy-group. The site of benzoylation was at C-1, as shown by the ^1H chemical shifts for H-1 (δ 6.50 and 6.44). The spectrum of the major component indicated that the

anomeric proton was equatorial (peak width 7 Hz) implying an α-configuration for the benzoate group, whereas in the minor component the H-1 signal appeared as a doublet of doublets ($J_{1,2ax}$ 10, $J_{1,2eq}$ 2 Hz) suggesting the β-configuration. In the latter compound, the



SCHEME

multiplet arising from the H-3, -4, -5, -6, and -6′ resonances was shifted 0.4 p.p.m. upfield to that of the major component. This indicates that in addition to having different anomeric configurations, the two compounds were also C-3 epimers. The structures of the major and minor components were therefore tentatively assigned as (6) and (7), whose precursors were evidently formed by the base-induced Michael addition of methanol to the rearranged products from the debenzoylation of (3)—(5) (see Scheme). In support of this mechanism, *aldehydo*-4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-*trans*-hex-2-enose (8) reacted with sodium methoxide to give a mixture of two products which had identical n.m.r. spectra to those of the products of (4) with sodium methoxide. The structure of (6) was confirmed by *X*-ray crystallographic techniques.

Crystal Structure of Compound (6).—The atom numbering scheme is shown in Figure 1, and a perspective view of

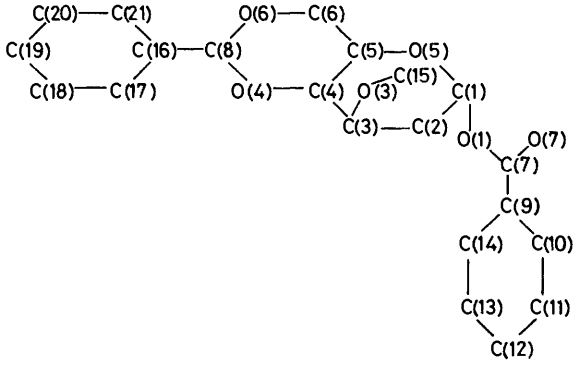


FIGURE 1 Structural formula and crystallographic numbering scheme of (6)

the molecule is shown in Figure 2: the molecular geometry and torsion angles are given in Tables 1 and 2. As expected, the dioxan and pyranose rings are *trans*-fused and in chair conformations. The pyranose ring adopts

TABLE 1

Molecular geometry

(a) Interatomic distances (Å)

C(1)–C(2)	1.51(2)	C(7)–O(7)	1.17(1)
C(2)–O(5)	1.42(1)	C(7)–C(9)	1.50(2)
C(1)–O(1)	1.45(1)	C(9)–C(10)	1.42(2)
C(2)–C(3)	1.52(1)	C(9)–C(14)	1.38(2)
C(3)–C(4)	1.50(2)	C(10)–C(11)	1.39(2)
C(3)–O(3)	1.42(1)	C(11)–C(12)	1.36(2)
C(4)–O(4)	1.45(1)	C(12)–C(13)	1.38(2)
C(4)–C(5)	1.53(2)	C(13)–C(14)	1.40(2)
O(4)–C(8)	1.44(1)	O(3)–C(15)	1.40(2)
C(5)–O(5)	1.45(1)	C(16)–C(17)	1.39(2)
C(5)–C(6)	1.51(2)	C(16)–C(21)	1.39(2)
C(6)–O(6)	1.41(1)	C(17)–C(18)	1.39(2)
O(6)–C(8)	1.42(1)	C(18)–C(19)	1.33(2)
C(8)–C(16)	1.50(2)	C(19)–C(20)	1.38(2)
O(1)–C(7)	1.38(2)	C(20)–C(21)	1.38(2)

(b) Interatomic angles (°)

C(2)–C(1)–O(5)	112(1)	O(1)–C(7)–O(7)	125(1)
C(2)–C(1)–O(1)	107(1)	O(1)–C(7)–C(9)	109(1)
O(1)–C(1)–O(5)	109(1)	O(7)–C(7)–C(9)	126(1)
C(1)–C(2)–C(3)	115(1)	C(7)–C(9)–C(10)	117(1)
C(2)–C(3)–C(4)	109(1)	C(7)–C(9)–C(14)	123(1)
C(2)–C(3)–O(3)	113(1)	C(10)–C(9)–C(14)	119(1)
C(4)–C(3)–O(3)	109(1)	C(9)–C(10)–C(11)	120(1)
C(3)–C(4)–O(4)	112(1)	C(10)–C(11)–C(12)	120(1)
C(3)–C(4)–C(5)	109(1)	C(11)–C(12)–C(13)	121(1)
O(4)–C(4)–C(5)	106(1)	C(12)–C(13)–C(14)	119(1)
C(4)–O(4)–C(8)	110(1)	C(13)–C(14)–C(9)	120(1)
C(4)–C(5)–O(5)	111(1)	C(3)–O(3)–C(15)	115(1)
C(4)–C(5)–C(6)	110(1)	C(8)–C(16)–C(17)	120(1)
O(5)–C(5)–C(6)	108(1)	C(8)–C(16)–C(21)	121(1)
C(1)–O(5)–C(5)	113(1)	C(17)–C(16)–C(21)	118(1)
C(5)–C(6)–O(6)	108(1)	C(16)–C(17)–C(18)	120(1)
C(6)–O(6)–C(8)	113(1)	C(17)–C(18)–C(19)	122(1)
O(4)–C(8)–O(6)	110(1)	C(18)–C(19)–C(20)	119(1)
O(4)–C(8)–C(16)	107(9)	C(19)–C(20)–C(21)	121(1)
O(6)–C(8)–C(16)	108(1)	C(20)–C(21)–C(16)	120(1)
C(1)–O(1)–C(7)	115(1)		

the $^4C_1$ conformation, placing the glycosidic bond in an axial orientation and the C(3) methoxy-substituent equatorial. The two fused rings are of the *trans*-decalin type, the angle between the planes 1 and 2 being only 2°. C(5) and C(8) are approximately equally displaced

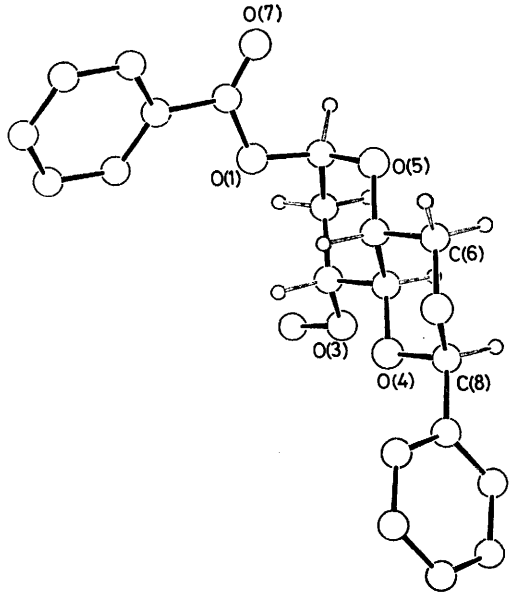


FIGURE 2 Structure of (6)

above and below the former plane. The flattening of the pyranose chair is reflected by the torsion angle O(5)–C(1)–C(2)–C(3) (48°) and the displacement of only 0.59 Å of C(1) from plane 1 (Table 3).

TABLE 2

Torsion angles (°) describing the conformation of the molecule

Endocyclic

O(5)–C(1)–C(2)–C(3)	48(1)	C(6)–O(6)–C(8)–O(4)	−62(1)
C(1)–C(2)–C(3)–C(4)	−50(1)	C(4)–O(4)–C(8)–O(6)	63(1)
C(2)–C(3)–C(4)–C(5)	55(1)	C(8)–O(4)–C(4)–C(5)	62(1)
C(3)–C(4)–C(5)–O(5)	−60(1)	O(4)–C(4)–C(3)–C(2)	172(1)
C(4)–C(5)–O(5)–C(1)	59(1)	O(4)–C(4)–C(5)–O(5)	179(1)
C(2)–C(1)–O(5)–C(5)	52(1)	C(6)–C(5)–C(4)–C(3)	180(1)
O(4)–C(4)–C(5)–C(6)	59(1)	O(6)–C(5)–O(5)–C(1)	180(1)
C(4)–C(5)–C(6)–O(6)	−57(1)	O(6)–C(6)–C(5)–O(5)	178(1)
C(5)–C(6)–O(6)–C(8)	58(1)	C(8)–O(4)–C(4)–C(3)	179(1)

Exocyclic

O(5)–C(1)–O(1)–C(7)	85(1)
O(1)–C(1)–C(2)–C(3)	−71(1)
O(1)–C(1)–O(5)–C(5)	66(1)
O(3)–C(3)–C(4)–O(4)	−64(1)
C(2)–C(3)–O(3)–C(15)	−61(1)
C(2)–C(1)–O(1)–C(7)	−154(1)
C(1)–C(2)–C(3)–O(3)	−171(1)
O(3)–C(3)–C(4)–C(5)	178(1)
C(4)–C(3)–O(3)–C(15)	178(1)
C(4)–O(4)–C(8)–C(16)	180(1)
C(6)–O(6)–C(8)–C(16)	−178(1)
C(1)–O(1)–C(7)–O(7)	3(1)
C(1)–O(1)–C(7)–C(9)	−176(1)

The average molecular geometry of the pyranose ring has been calculated using the results of 27 structure determinations,[6] and the values may be compared with those observed here. All C–C bond lengths are within one estimated standard deviation of the mean value of 1.523 Å, and C–O bond lengths [excluding those to O(1) and O(5)] within two estimated standard deviations of the mean value of 1.426 Å. The observed C(5)–O(5) distance [1.45(1) Å] does not differ significantly from the mean value of 1.436 Å. In the averaged structure differing bond lengths are observed in the O(5)–C(1)–O(1)–R system depending upon the configuration of C(1) and the nature of R, but the lack of precision in our structure determination precludes any useful discussion of these details. The averaged ring bond angles at carbon atoms are all similar with mean values between 109.2 and 110.3°; in this present structure only C(1)–C(2)–C(3) [115(1)°] differs significantly from this range of values, possibly reflecting the absence of a substituent on C(2).

TABLE 3

Least-squares planes

The equation of the planes are of the form $PX + QY + RZ = S$, where X, Y, and Z are fractional co-ordinates referred to unit orthogonal axes

Plane	Atoms defining the plane	P	Q	R	S
1	C(4), O(4), C(6), O(6)	0.5596	−0.5822	0.5898	4.5429
2	C(2), C(3), C(5), O(5)	0.5681	−0.5507	0.6115	5.5338
3	C(9)—C(14)	−0.2514	0.8231	0.5093	1.3707
4	C(16)—C(21)	0.8385	−0.2376	−0.4904	1.0433

Distances of atoms from the planes (Å)

Plane 1		Plane 2		Plane 3		Plane 4	
C(3)	0.68	C(1)	0.57	O(7)	−0.28	C(16)	0.01
C(4)	−0.02	C(2)	0.02	C(7)	0.04	C(17)	0.01
C(5)	0.71	C(3)	−0.02	C(9)	−0.01	C(18)	−0.01
C(6)	0.02	C(4)	−0.69	C(10)	−0.01	C(19)	0.01
O(6)	−0.02	C(5)	0.02	C(11)	0.01	C(20)	0.01
C(8)	−0.68	O(5)	−0.02	C(12)	−0.01	C(21)	−0.01
O(4)	0.02	C(6)	−0.64	C(13)	−0.01		
				C(14)	0.02		

Angles between the planes (°): 1–2 = 2, 1–3 = 109, 1–4 = 71, 2–3 = 106, 2–4 = 72, 3–4 = 131

It is therefore concluded that (6) is 1-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-α-D-*arabino*-hexose and (7) is 1-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-β-D-*ribo*-hexose. The exclusive adoption of the β-configuration in (7) may possibly indicate that the 1,3-interaction between the 3-methoxy-group and the anomeric benzoate group in the alternative α-configuration is of sufficient magnitude to overcome the anomeric effect.

4,6-*O*-Benzylidene-D-glucal (1) also underwent reaction with benzoic acid, TPP, and DEAD, to give compound (3) in high yield as the sole product.

EXPERIMENTAL

General.—M.p.s are uncorrected. Optical rotations were measured for $CHCl_3$ solutions on a Perkin-Elmer 241 polarimeter. ^{1}H N.m.r. spectra (60 MHz; internal Me_4Si) were recorded with a Varian EM-360 spectrometer. ^{13}C N.m.r. spectra (22.628 MHz) were recorded with a Bruker HX-90 spectrometer. P.l.c. was performed on Kieselgel GF 254 (Merck), and detection was effected by iodine vapour or u.v. light (254 nm).

3-O-*Benzoyl*-4,6-O-*benzylidene*-D-*glucal* (5).—To a solution of 4,6-*O*-benzylidene-D-glucal (1) (264 mg, 1 mmol) in pyridine (5 ml) at 0° was added benzoyl chloride (0.13 ml, 1.1 equiv.) with stirring. The mixture was kept at 0° for 1 h, and then poured onto ice whereupon the *title compound* crystallized. Filtration and recrystallization from ethanol afforded needles (325 mg, 96%), m.p. 146—147°, $[\alpha]_D^{23}$ −40.2° (*c* 1.00), δ 8.05 (2 H, m, benzoate aromatic protons), 7.05—7.60 (8 H, m, benzylidene and benzoate aromatic protons), 6.45 (1 H, dd, H-1, $J_{1,2}$ 6.0, $J_{1,3}$ 1.5 Hz), 5.80 (1 H, ddd, H-3, $J_{2,3}$ 2.3, $J_{3,4}$ 6.0 Hz), 5.60 (1 H, s, PhC*H*), 4.90 (1 H, dd, H-2), and 3.60—4.55 (4 H, m, H-4-, 5-, -6ax, -6eq) (Found: C, 70.9; H, 5.3. $C_{20}H_{18}O_5$ requires C, 71.0, H, 5.4%).

Reaction of 4,6-O-*Benzylidene*-D-*allal* (2) *with Triphenylphosphine, Benzoic Acid, and DEAD.*—To a solution of compound (2) [7] (234 mg, 1 mmol) and triphenylphosphine (525 mg, 2 equiv.) and benzoic acid (244 mg, 2 equiv.) in THF (5 ml) was added dropwise a solution of DEAD (312 μl, 2 equiv.) in THF (1 ml). The mixture was stirred at room temperature for 1 h, the solvent evaporated, and the residue dissolved in dichloromethane (25 ml) and washed successively with saturated sodium hydrogencarbonate solution and water. After evaporation of the solvent from the organic phase, the residue was chromatographed (p.l.c.; acetone–hexane, 1 : 4) to give unchanged starting material (58.5 mg, 25%) and a mixture of compounds which crystallized upon trituration with ether. Recrystallization from aqueous acetone afforded needles of 1-O-*benzoyl*-4,6-O-*benzylidene*-2,3-*dideoxy*-α-D-erythro-*hex*-2-*enopyranose* (3)

(122 mg, 36%), m.p. 125—126°, $[\alpha]_D^{25}$ +149° (*c* 0.98), δ 8.03—8.28 (2 H, m, benzoyl aromatic protons), 7.33—7.70 (8 H, m, benzoyl + benzylidene aromatic protons), 6.73 (1 H, m, H-1), 6.35 (1 H, ddd, H-3, $J_{2,3}$ 10 Hz), 5.82 (1 H, dt, H-2, $J_{1,2} = {}^4J_{2,4} = 2.0$ Hz), 5.63 (1 H, s, H-7), and 3.80—4.65 (4 H, m, H-4, -5, -6ax, -6eq), δ_C 102.2 (PhCH), 91.7 (C-1), 74.6 (C-4), 71.4 (C-5), 68.9 (C-6), 125.0, 125.2, 128.3, 128.4, 129.2, 130.0, 131.3, 132.9, and 133.5 p.p.m. (aromatics, C-2, C-3) (Found: C, 70.9; H, 5.5. $C_{20}H_{18}O_5$ requires C, 71.0; H, 5.4%).

The mother liquors were treated with methanol (20 ml) containing sodium (*ca.* 2 mg) for 16 h at room temperature. After neutralization with solid carbon dioxide, the solvent was evaporated and the residue extracted with warm ethyl acetate. The concentrated extract was subjected to chromatography (p.l.c.; acetone–hexane, 1 : 4) to give two bands, the more mobile of which contained 4,6-*O*-benzylidene-D-glucal (1) (21 mg, 9%), indistinguishable from an authentic sample by comparison of physical and spectral properties. The less mobile band (92 mg, 25%) contained a mixture of two compounds which could not be resolved by further chromatography. This mixture was dissolved in pyridine (3 ml) and treated with benzoyl chloride (0.5 ml) at 0° for 24 h. Work-up and chromatography (p.l.c.; acetone–hexane 1 : 9; four consecutive developments) afforded two compounds. The major component was 1-O-*benzoyl*-4,6-O-*benzylidene*-2-*deoxy*-3-O-*methyl*-α-D-arabino-*hexopyranose* (6) which crystallized from aqueous propan-2-ol to yield prisms, m.p. 122—122.5°, $[\alpha]_D^{24}$ +93.2° (*c* 0.71), δ 8.00—8.20 (2 H, m, benzoate aromatic protons), 7.20—7.65 (8 H, m, benzoate and benzylidene aromatic protons), 6.80 (1 H, m, H-1), 5.65 (1 H, s, H-7), 3.50—4.47 (5 H, m, H-3, -4, -5, -6ax, -6eq), 3.59 (3 H, s, OCH_3), and 1.80—2.62 (2 H, m, H-2ax, -2eq) (Found: C, 68.2; H, 6.1. $C_{21}H_{22}O_6$ requires C, 68.1; H, 6.0%).

The minor component was 1-O-*benzoyl*-4,6-O-*benzylidene*-2-*deoxy*-3-O-*methyl*-β-D-ribo-*hexopyranose* (7). Recrystallization from aqueous propan-2-ol afforded needles, m.p. 115—117°, $[\alpha]_D^{24}$ −16.6° (*c* 0.35), δ 8.00—8.25 (2 H, m, benzoate aromatic protons), 7.24—7.67 (8 H, m, benzoate and benzylidene aromatic protons), 6.10 (1 H, dd, H-1, $J_{1,2ax}$ 10, $J_{1,2eq}$ 2.2 Hz), 3.50—4.55 (5 H, m, H-3, -4, -5, -6ax, -6eq), 3.52 (3 H, s, OCH_3), and 1.70—2.76 (2 H, m, H-2ax, -2eq) (Found: C, 68.4; H, 6.1. $C_{21}H_{22}O_6$ requires C, 68.1; H, 6.0%).

Reaction of 4,6-O-*Benzylidene*-D-*glucal* (1) *with Triphenylphosphine, Benzoic Acid, and DEAD.*—To a solution of compound (1) (78 mg), triphenylphosphine (175 mg), and benzoic acid (81.3 mg) in THF (2 ml) was added dropwise a solution of DEAD (104 μl) in THF (0.5 ml), and the mixture stirred for 1 h at room temperature. Work-up and p.l.c., as described above, afforded 1-*O*-benzoyl-4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranose (3) (103 mg, 92%) as the sole product.

Reaction of aldehydo-4,6-O-*Benzylidene*-2,3-*dideoxy*-D-erythro-*hex*-2-*enose* (8) *with Sodium Methoxide.*—A solution of compound (8) [8] (50 mg) in methanol (10 ml) was treated with sodium (1 mg) for 4 h at room temperature. After neutralization with solid carbon dioxide and evaporation of the solvent, the residue was extracted with warm ethyl acetate. P.l.c. (acetone–hexane 1 : 3) afforded a mixture of two compounds (58 mg, 96%) which upon treatment with benzoyl chloride (0.2 ml) in pyridine (2 ml) at 0° for 24 h and p.l.c. (acetone–hexane 1 : 9; 4 consecutive developments) gave compounds (6) and (7).

X-*Ray Crystallography.*—*Crystal data.* 1-*O*-Benzoyl-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-α-D-*arabino*-hexose (6), $C_{21}H_{22}O_6$, $M_r = 370.3$, $F(000) = 784$, orthorhombic, $P2_12_12_1$, $a = 21.789(2)$, $b = 14.772(3)$, $c = 5.925(2)$ Å, $U = 1\,907.1$ Å^3, $Z = 4$, $D_c = 1.288$ g cm^{-3}, μ(Mo-K_α) = 0.057 mm^{-1}.

Crystallographic Measurements.—Crystals were grown at room temperature from an aqueous propan-2-ol solution. A crystal *ca.* 0.24 × 0.12 × 0.13 mm was selected for data collection. Cell dimensions and intensities were measured on a Philips PW1100 diffractometer with graphite-monochromated Mo-K_α radiation using an ω–2θ scan. 1953 Reflexions were measured in the range $1.0 \leqslant \theta \leqslant 25.0°$ of which 825 with $I \geqslant 2\sigma(I)$ were used in the structure refinement.

The number of observed reflexions was adequate to determine the structure and stereochemistry, although the

TABLE 4

Fractional co-ordinates

(a) Non-hydrogen atoms (× 10^4)

	x	*y*	*z*
C(1)	3 220(6)	1 100(9)	8 323(24)
C(2)	3 605(6)	1 606(9)	6 626(23)
C(3)	3 889(6)	2 480(8)	7 491(24)
C(4)	3 396(6)	3 037(8)	8 578(24)
O(4)	3 648(4)	3 820(6)	9 720(16)
C(5)	3 074(6)	2 474(9)	10 390(25)
O(5)	2 793(4)	1 675(6)	9 423(16)
C(6)	2 577(6)	3 030(9)	11 509(27)
O(6)	2 855(4)	3 820(6)	12 390(17)
C(8)	3 159(6)	4 324(8)	10 708(26)
O(1)	3 637(3)	0 724(5)	9 971(15)
C(7)	3 433(6)	−0 042(11)	11 058(26)
O(7)	2 970(4)	−0 414(6)	10 682(18)
C(9)	3 894(6)	−0 304(8)	12 809(23)
C(10)	3 683(6)	−0 845(8)	14 626(22)
C(11)	4 085(6)	−1 081(9)	16 342(25)
C(12)	4 680(7)	−0 805(9)	16 273(28)
C(13)	4 897(6)	−0 277(9)	14 518(26)
C(14)	4 495(6)	−0 011(9)	12 796(26)
O(3)	4 169(5)	3 004(6)	5 771(17)
C(15)	4 658(10)	2 582(12)	4 645(37)
C(16)	3 446(5)	5 144(9)	11 845(23)
C(17)	3 441(6)	5 985(10)	10 807(28)
C(18)	3 738(7)	6 713(12)	11 832(31)
C(19)	4 039(6)	6 628(11)	13 777(26)
C(20)	4 043(6)	5 795(9)	14 828(29)
C(21)	3 748(5)	5 057(9)	13 893(23)

(b) Hydrogen atoms (× 10^3)

	x	*y*	*z*
H(1)	296	058	747
H(21)	397	116	609
H(22)	332	177	520
H(3)	424	229	867
H(4)	309	325	726
H(5)	342	227	1 161
H(61)	237	265	1 286
H(62)	223	321	1 028
H(8)	283	454	943
H(10)	321	−107	1 467
H(11)	393	−148	1 774
H(12)	499	−100	1 761
H(13)	537	−007	1 448
H(14)	465	042	1 146
H(151)	500(6)	219(8)	578(21)
H(152)	456(6)	201(8)	406(25)
H(153)	490(6)	308(8)	393(21)
H(17)	321	608	923
H(18)	372	737	1 102
H(19)	427	720	1 452
H(20)	428	572	1 641
H(21)	375	441	1 476

use of Cu-K_α radiation would have been preferable if a detailed study of the molecular geometry had been required.

Structure solution and refinement. The structure was solved by direct methods.[9] *E*-Maps were calculated using 229 reflexions with $E \geqslant 1.4$; the map which was ranked fourth using a combined figure-of-merit showed the positions of 26 out of 27 heavy atoms. The remaining carbon atom was located from a subsequent difference synthesis. Isotropic full-matrix least-squares refinement (R 0.14) followed by a difference map showed the positions of 17 out of 22 hydrogen atoms. Owing to the shortage of data the hydrogen atoms were included in calculated positions (C–H 1.08 Å) and refined using a riding model. This treatment was not satisfactory for the C(15) methyl group, the hydrogen atoms of which were included in positions obtained from a difference map and refined with C–H distances constrained to 1.080(5) Å. A common isotropic temperature factor was refined for all the hydrogen atoms [0.072(9) Å^2]. Atoms O(7), O(3), and C(15) were refined anisotropically since these had associated ripples of electron density on a difference map when refined isotropically. The final refinement converged at R 0.095, R_w 0.084 ($R = \Sigma\Delta/\Sigma|F_o|$, $R_w = \Sigma_w{}^{\frac{1}{2}}\Delta/\Sigma_w{}^{\frac{1}{2}}|F_o|$). The fractional atomic coordinates of the heavy atoms are given in Table 4.*

* Lists of structure factors and thermal parameters are in Supplementary Publication No. SUP 22995 (7 pp.). For details, see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1979, Index issue.

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