Carbohydrate Research, 216 (1991) 11–20
Elsevier Science Publishers B.V., Amsterdam

The crystallographic conformations of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*- and -β-L-*glycero*-D-*galacto*-oct-7-enopyranose*†

John C. Barnes and John S. Brimacombe‡
Department of Chemistry, The University of Dundee, Dundee DD1 4HN (Great Britain)

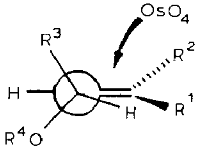
(Received January 24th, 1991; accepted for publication February 14th, 1991)

ABSTRACT

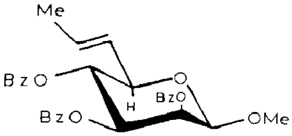
In the crystal structure of both 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-oct-7-enopyranose (**8**) and the corresponding β-L-*glycero*-D-*galacto* isomer **9**, the allylic system adopts an essentially eclipsed conformation with the smallest group, H-6, at the adjacent stereocentre eclipsing the olefinic double bond. The torsion angle H-6–C-6–C-7–C-8 is −5.7° for **8** and −14.1° for **9**. Based on the crystallographic conformations, an attempt has been made to account for the widely different facial selectivities of **8** and **9** towards catalytic osmylation.

INTRODUCTION

Based on the known preference of allylic systems to adopt an eclipsed conformation[2,3], and assuming that this preference persists in the transition state, Kishi and his co-workers[4] proposed that the stereoselectivities observed in their osmylation reactions resulted from preferential attack of OsO_4 on the face of the olefinic double bond opposite to that of the pre-existing hydroxyl (or alkoxyl) group when the molecule adopts the least-compressed conformation **1**. This and several other models[5–7] used to predict the stereochemical outcome of the osmylation of chiral allylic systems are based on reactant-like transition states that require some knowledge of the ground-state conformation of the unsaturated substrates.



1



2

---

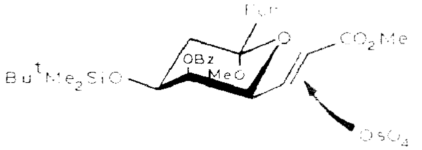
* Dedicated to Professor Grant Buchanan on the occasion of his 65th birthday.

† Higher-carbon Sugars, Part 16. For Part 15, see ref. 1.

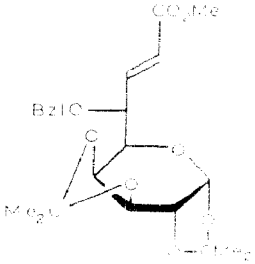
‡ To whom correspondence should be addressed.

0008-6215/91/$03.50

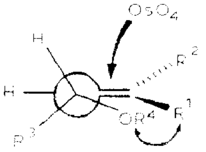
Valuable information about the ground-state conformation can be obtained by X-ray crystallography, and allows the crystallographic ground-state conformations of allylic systems to be compared with those used in various models. Such studies have shown[5] that the C-5–H bond does indeed eclipse the olefinic double bond in the ground-state conformation of the (*E*)-heptenopyranoside derivative **2**, which undergoes a highly stereoselective osmylation[8] in conformity with Kishi's formulation[4]. On the other hand, crystallographic studies have provided clear evidence that (*E*)-conjugate esters, such as **3**[5] and **4**[9], adopt the synperiplanar (or "alkoxy-inside"[6]) conformation **5** advocated by Stork and Kahn[7], with virtual eclipsing of the allylic C–O and olefinic bonds. Approach of OsO_4 to the olefinic bond on the less-hindered face readily rationalises the facial selectivities observed with these systems[5,9] on *syn*-hydroxylation.



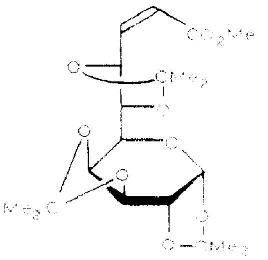
3 Fur = furan-2-yl



4



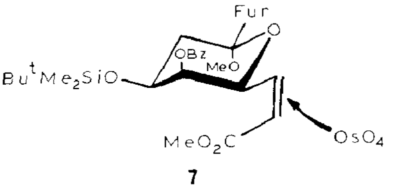
5



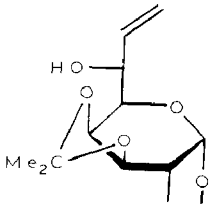
6

The situation is less clear-cut with (*Z*)-conjugate esters, which sometimes violate[5,10] Kishi's formulation[4], despite the expectation that they should exhibit a strong preference for the conformation **1** (R^1 = CO_2alkyl, R^2 = H) in which the smallest group at the adjacent stereocentre eclipses the olefinic double bond. This eclipsed conformation is found in the crystal structure of the (*Z*)-decenopyranuronate **6**[9], which for steric reasons exhibited[11] virtually no facial selectivity, whereas the (*Z*)-conjugate ester **7** adopts an antiperiplanar arrangement of the allylic C–O and olefinic bonds in the solid state[5], and undergoes stereospecific osmylation from the less-hindered α-face to give[12] the anti-Kishi product.

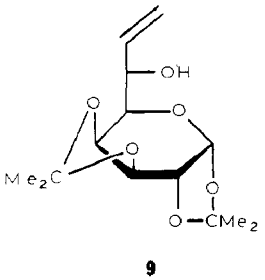
Despite the theoretical limitations[13] imposed by using the ground-state conformation to predict the stereochemical outcome of reactions, there is a strong correlation[5,9] between the crystallographic ground-state conformations of several alkenylpyranosides and the stereochemical outcome of their reactions with OsO_4. This encouraged us to look at other examples, notably those of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-oct-7-enopyranose (**8**) (ref. 14) and its C-6 epimer **9** (ref. 15). Although both epimers undergo catalytic osmylation in keeping with Kishi's model[4], the facial stereoselectivity for that of **8** (>20:1) (ref. 16) is much superior to that of **9** (~3:1) (ref. 15). It was of interest to know whether differences in their ground-state conformations were responsible for this disparity.



7



8



9

RESULTS AND DISCUSSION

The X-ray structure of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-oct-7-enopyranose (**8**) (ref. 14) is shown in Fig. 1 (see Experimental section for

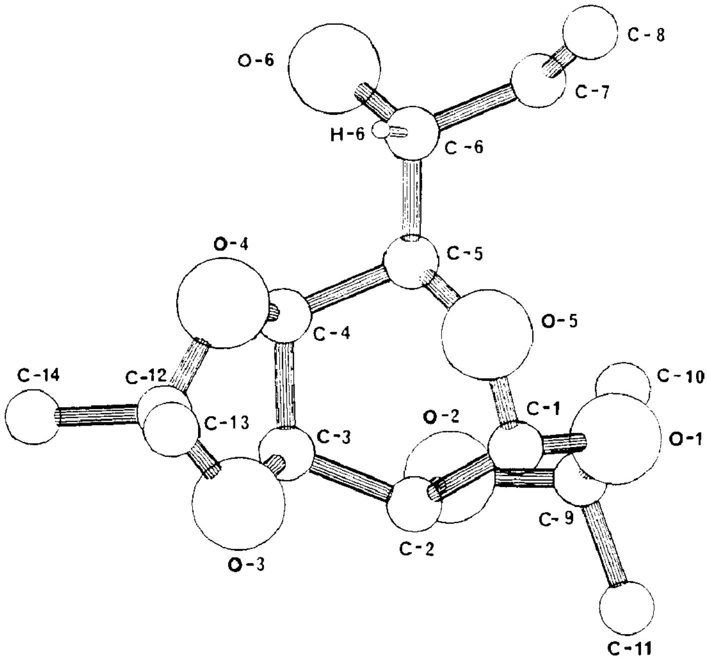


Fig. 1. Conformation of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-oct-7-enopyranose (**8**), with the numbering scheme used.

TABLE I

Fractional co-ordinates (× 10^4)[a] and equivalent isotropic temperature factors (× 10^3)[b] for **8**

Atom	x/a	y/b	z/c	U_{eq}
C-1	−8335(3)	−4168(5)	−11884(4)	39(1)
C-2	−7311(3)	−4870(5)	−10582(4)	38(1)
C-3	−6202(3)	−4431(5)	−10937(4)	36(1)
C-4	−6141(3)	−2610(5)	−11650(4)	36(1)
C-5	−7250(3)	−1689(5)	−11986(4)	35(1)
C-6	−7284(3)	−73(5)	−13070(4)	39(1)
C-7	−8372(3)	845(5)	−13324(5)	48(1)
C-8	−8996(4)	1317(6)	−14818(6)	71(1)
C-9	−8516(3)	−3915(6)	−9047(5)	47(1)
C-10	−8642(4)	−2351(7)	−8012(6)	67(1)
C-11	−8947(4)	−5532(7)	−8388(6)	68(1)
C-12	−5461(3)	−4557(5)	−13311(5)	44(1)
C-13	−5806(4)	−5161(7)	−15136(5)	73(1)
C-14	−4210(3)	−4677(6)	−12515(6)	64(1)
O-1	−9044(2)	−3659(4)	−10836(3)	50(1)
O-2	−7359(2)	−4089[c]	−9000(3)	42(1)
O-3	−6040(2)	−5514(4)	−12281(4)	47(1)
O-4	−5842(2)	−2862(4)	−13232(3)	50(1)
O-5	−8117(2)	−2806(4)	−12889(3)	39(1)
O-6	−6396(2)	930(4)	−12090(4)	57(1)

[a] Estimated standard deviations in parentheses. [b] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$. [c] Fixed co-ordinate.

TABLE II

Bond lengths[a] (Å) for **8**

Bond		*Bond*	
C-1–C-2	1.517(5)	C-6–C-7	1.482(5)
C-1–O-1	1.398(5)	C-6–O-6	1.405(4)
C-1–O-5	1.382(4)	C-7–C-8	1.293(5)
C-2–C-3	1.496(5)	C-9–C-10	1.486(6)
C-2–O-2	1.403(4)	C-9–C-11	1.498(6)
C-3–C-4	1.521(5)	C-9–O-1	1.418(4)
C-3–O-3	1.404(4)	C-9–O-2	1.420(4)
C-4–C-5	1.501(5)	C-12–C-13	1.476(5)
C-4–O-4	1.402(4)	C-12–C-14	1.514(5)
C-5–C-6	1.507(5)	C-12–O-3	1.415(4)
C-5–O-5	1.418(4)	C-12–O-4	1.394(5)

[a] Estimated standard deviations in parentheses.

crystal data and other information), together with the crystallographic numbering. Refined fractional co-ordinates are given in Table I, bond lengths in Table II, and bond angles and selected torsion angles in Table III. The significant structural features of the exocyclic side-chain of **8** are seen in Fig. 1, which shows that the allylic system adopts an

TABLE III

Bond angles and selected torsion angles[a] (degrees) for **8**

Bond angles			
C-2–C-1–O-1	103.4(3)	C-6–C-7–C-8	124.8(4)
C-2–C-1–O-5	114.5(3)	C-10–C-9–C-11	112.9(3)
O-1–C-1–O-5	111.4(3)	C-10–C-9–O-1	110.7(3)
C-1–C-2–C-3	115.7(3)	C-10–C-9–O-2	107.6(3)
C-1–C-2–O-2	104.0(3)	C-11–C-9–O-1	110.4(3)
C-3–C-2–O-2	108.2(3)	C-11–C-9–O-2	110.5(3)
C-2–C-3–C-4	114.1(3)	O-1–C-9–O-2	104.4(3)
C-2–C-3–O-3	108.3(3)	C-13–C-12–C-14	113.9(3)
C-4–C-3–O-3	103.8(3)	C-13–C-12–O-3	109.5(3)
C-3–C-4–C-5	112.1(3)	C-13–C-12–O-4	108.7(3)
C-3–C-4–O-4	104.5(3)	C-14–C-12–O-3	109.4(3)
C-5–C-4–O-4	109.5(3)	C-14–C-12–O-4	110.9(3)
C-4–C-5–C-6	112.9(3)	O-3–C-12–O-4	103.9(3)
C-4–C-5–O-5	109.8(3)	C-1–O-1–C-9	110.8(3)
C-6–C-5–O-5	107.7(3)	C-2–O-2–C-9	106.2(3)
C-5–C-6–C-7	111.7(3)	C-3–O-3–C-12	108.2(3)
C-5–C-6–O-6	103.4(3)	C-4–O-4–C-12	109.6(3)
C-7–C-6–O-6	111.4(3)	C-1–O-5–C-5	113.6(3)
Torsion angles			
C-5–C-6–C-7–C-8	−127.9(4)	O-6–C-6–C-7–C-8	117.0(4)
H-6–C-6–C-7–C-8	−5.7(6)		

[a] Estimated standard deviations in parentheses.

eclipsed conformation akin to **1** ($R^1 = R^2 = H$) with the smallest group, H-6, eclipsing the olefinic double bond (H-6–C-6–C-7–C-8 −5.7°). Other features of the structure are unexceptional.

The X-ray structure of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-oct-7-enopyranose (**9**) (ref. 15) is shown in Fig. 2 (see Experimental section for crystal data and other information), together with the crystallographic numbering. Refined fractional co-ordinates are given in Table IV, bond lengths in Table V, and bond angles and selected torsion angles in Table VI. Inspection of Fig. 2 reveals that the H-6–C-6 bond again nearly eclipses the olefinic double bond, with a torsion angle (H-6–C-6–C-7–C-8 −14.1°) slightly larger than that found in **8**.

The eclipsed conformation having the smallest group at the adjacent stereocentre eclipsing the olefinic double bond would be favoured on steric grounds. For the eclipsed conformations depicted in Figs. 1 and 2, the major isomer produced on catalytic osmylation of each of **8** and **9** would result from attack of OsO_4 on the olefinic double bond from the direction anti to the allylic oxygen atom at C-6 (Kishi model[4]). In attempts to develop less empirical models, electronic[5,7] and steric effects[4,9] have each been invoked in predicting the preferred transition-state geometry of allylic systems undergoing osmylation, and a model more "product-like" than Kishi's, which considers primarily the steric interactions between the incoming electrophile and the allylic system, has also been proposed[17].

TABLE IV

Fractional co-ordinates ($\times 10^4$)[a] and equivalent isotropic temperature factors ($\times 10^3$)[b] for **9**

Atom	x/a	y/b	z/c	U_{eq}
C-1	−2556(16)	9275(5)	6330(6)	53(1)
C-2	−1464(15)	9132(5)	5374(6)	48(1)
C-3	−175(16)	9790(5)	4926(6)	55(2)
C-4	915(16)	10314(5)	5660(5)	50(1)
C-5	513(15)	10070(5)	6698(7)	51(1)
C-6	1101(16)	10669(6)	7434(6)	54(1)
C-7	3560(15)	10829(6)	7371(7)	60(2)
C-8	4457(18)	11445(7)	7002(7)	76(2)
C-9	−817(17)	8125(5)	6305(6)	55(2)
C-10	1042(18)	7817(6)	6920(9)	79(2)
C-11	−2255(19)	7512(5)	5918(7)	70(2)
C-12	−1085(17)	11022(5)	4596(6)	56(1)
C-13	652(18)	11233(6)	3843(6)	65(2)
C-14	−3106(18)	11533(7)	4588(9)	84(2)
O-1	−2075(12)	8632(4)	6859(4)	64(1)
O-2	121(10)	8568(3)	5588(4)	54(1)
O-3	−1750(11)	10270(4)	4462(5)	63(1)
O-4	−99(11)	11033(3)	5506(4)	59(1)
O-5	−1790(9)	9929(3)	6811(4)	52(1)
O-6	671(12)	10386(4)	8344(4)	66(1)

[a] Estimated standard deviations in parentheses. [b] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

TABLE V

Bond lengths[a] (Å) for **9**

Bond		*Bond*	
C-1–C-2	1.525(12)	C-6–C-7	1.500(14)
C-1–O-1	1.406(10)	C-6–O-6	1.409(11)
C-1–O-5	1.430(10)	C-7–C-8	1.333(14)
C-2–C-3	1.544(12)	C-9–C-10	1.516(14)
C-2–O-2	1.418(10)	C-9–C-11	1.498(13)
C-3–C-4	1.545(12)	C-9–O-1	1.417(11)
C-3–O-3	1.435(11)	C-9–O-2	1.406(10)
C-4–C-5	1.554(13)	C-12–C-13	1.536(13)
C-4–O-4	1.439(10)	C-12–C-14	1.516(14)
C-5–C-6	1.538(13)	C-12–O-3	1.417(11)
C-5–O-5	1.408(11)	C-12–O-4	1.419(11)

[a] Estimated standard deviations in parentheses.

Since electronic effects associated with the allylic system would be much the same for both **8** and **9**, it seems reasonable to account for the disparity between their facial selectivities towards osmylation by considering how other parts of the molecule might affect the approach of a large electrophile like OsO_4 to the olefinic double bond and,

TABLE VI

Bond angles and selected torsion angles[a] (degrees) for **9**

Bond angles			
C-2-C-1-O-1	104.4(7)	C-6-C-7-C-8	125.1(11)
C-2-C-1-O-5	115.1(7)	C-10-C-9-C-11	111.5(8)
O-1-C-1-O-5	110.5(7)	C-10-C-9-O-1	107.6(7)
C-1-C-2-C-3	116.8(7)	C-10-C-9-O-2	109.2(8)
C-1-C-2-O-2	102.5(7)	C-11-C-9-O-1	111.6(8)
C-3-C-2-O-2	107.4(7)	C-11-C-9-O-2	112.2(7)
C-2-C-3-C-4	113.4(7)	O-1-C-9-O-2	104.5(7)
C-2-C-3-O-3	108.6(7)	C-13-C-12-C-14	112.6(8)
C-4-C-3-O-3	102.8(7)	C-13-C-12-O-3	109.3(8)
C-3-C-4-C-5	113.7(7)	C-13-C-12-O-4	110.4(8)
C-3-C-4-O-4	105.3(7)	C-14-C-12-O-3	110.5(8)
C-5-C-4-O-4	109.3(7)	C-14-C-12-O-4	109.2(8)
C-4-C-5-C-6	114.3(7)	O-3-C-12-O-4	104.5(7)
C-4-C-5-O-5	108.1(8)	C-1-O-1-C-9	109.8(7)
C-6-C-5-O-5	105.7(8)	C-2-O-2-C-9	106.9(6)
C-5-C-6-C-7	108.5(8)	C-3-O-3-C-12	108.9(7)
C-5-C-6-O-6	109.2(8)	C-4-O-4-C-12	107.5(6)
C-7-C-6-O-6	107.5(8)	C-1-O-5-C-5	113.9(7)
Torsion angles			
C-5-C-6-C-7-C-8	106.5(10)	O-6-C-6-C-7-C-8	135.5(10)
H-6-C-6-C-7-C-8	−14.1(14)		

[a] Estimated standard deviations in parentheses.

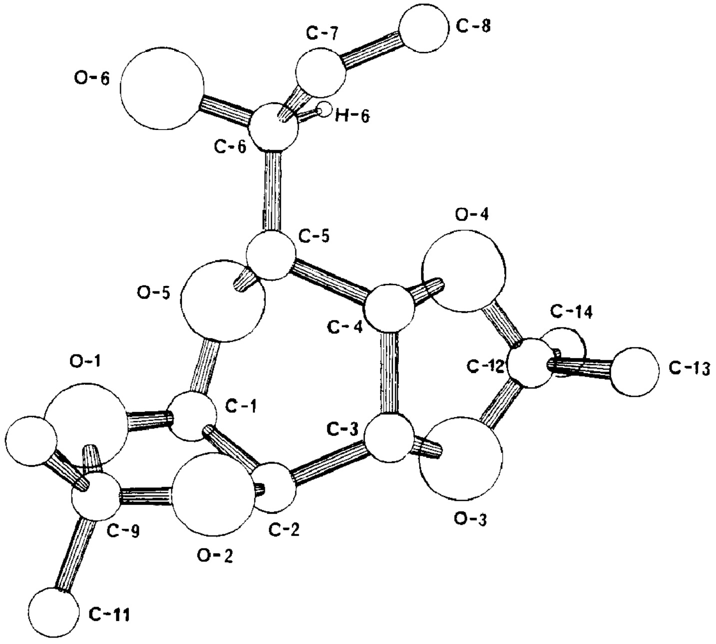


Fig. 2. Conformation of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*glycero*-D-*galacto*-oct-7-enopyranose (**9**), with the numbering scheme used.

consequently, non-bonded interactions generated in the transition state. This can only be done in a rather sketchy way since the reaction pathway for osmylation is not well understood[18]. In view of the high stereoselectivity encountered[16] with **8**, it follows that OsO_4 has relatively unimpeded access to the olefinic double bond from the direction anti to O-6 in the eclipsed conformation shown in Fig. 1, so that any non-bonded interactions engendered in the transition state should impose little restraint. With **9**, the approach of OsO_4 on the opposite side to O-6 (see Fig. 2) is restricted to some extent by the 3,4-*O*-isopropylidene group, resulting in an increase in the non-bonded interactions in the transition state and a consequent reduction in facial selectivity. Similar considerations would hold for models emanating from the eclipsed conformations shown in Figs. 1 and 2, but which are more "product-like".

EXPERIMENTAL

Crystal data for **8**[14]. — $C_{14}H_{22}O_6$; $M = 286.32$; monoclinic, space group $P2_1$; $a = 12.290(2)$, $b = 7.708(3)$, $c = 7.911(2)$ Å; $\beta = 104.26(2)^\circ$; volume $= 726.33$ Å^3, $D_c = 1.31$ g.cm^{-3}, $Z = 2$, $F(000) = 308$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu = 0.63$ cm^{-1}.

Crystal data for **9**[15]. — $C_{14}H_{22}O_6$; $M = 286.32$; orthorhombic, space group $P2_12_12_1$; $a = 5.976(5)$, $b = 17.910(6)$, $c = 14.180(1)$ Å; volume $= 1517.69$ Å^3, $D_c = 1.25$ g.cm^{-3}, $Z = 4$, $F(000) = 616$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu = 0.63$ cm^{-1}.

Data collection. — After preliminary photographs, data for both compounds were collected on a Stoe Stadi II diffractometer. The crystals showed no significant change in the intensities of standard reflections during data collection. The structures were solved by direct methods, which yielded all of the carbon and oxygen atoms, and refined by conventional least-squares and difference-synthesis procedures. In the final cycles of refinement, carbon and oxygen atoms were assigned anisotropic temperature parameters, and hydrogen atoms were introduced at calculated positions with isotropic temperature parameters either fixed (for **8**) or refined in groups (for **9**).

Structure analysis for **8** (Tables I–III). — Cell dimensions were refined from 15 carefully centred reflections ($\theta \sim 12^\circ$) with a crystal measuring approximately $0.20 \times 0.35 \times 0.43$ mm mounted along the *b* axis. Data were collected over the range $1 \leq \theta \leq 25^\circ$. From the 1591 reflections measured, 1283 unique data ($R_{int} = 0.014$) were obtained; 1182 reflections with $F_o \geq 3\sigma(F)$ were used in further refinements. Range of indices: $-14 \leq h \leq 14, 0 \leq k \leq 7, 0 \leq l \leq 9$. After refinement (187 parameters and minimising $\Sigma w|F_o - |F_c||^2$), the *R* factor was 0.045 and the weighted *R* factor was 0.057; the weighting scheme used was $w = 1.4272/[\sigma^2(F) + 0.001008\ F^2]$. In the final cycles of refinement, the maximum shift/e.s.d. was 0.490 and the average shift/e.s.d. was 0.062. The final difference-electron-density synthesis showed maximum and minimum electron densities of 0.169 and −0.182 e.Å^{-3}, respectively.

The formation of a hydrogen bond O-6···O-3′ (where O-3′ is part of the molecule at $x, y-1, z$), leads to the space group $P2_1$ instead of the usually observed space group $P2_12_12_1$.

Structure analysis for **9** (Tables IV–VI). — Cell dimensions were refined from 20 carefully centred reflections ($\theta \sim 12°$) with a crystal measuring approximately 0.54 × 0.33 × 0.27 mm mounted along the *a* axis. Data were collected over the range $1 \leq \theta \leq 25°$. From the 2306 reflections measured, 1324 unique data ($R_{int} = 0.029$) were obtained; 1047 reflections with $F_o \geq 3\sigma(F)$ were used in further refinements. Range of indices $0 \leq h \leq 5, 0 \leq k \leq 21, -16 \leq l \leq 16$. After refinement (187 parameters and minimising $\Sigma w|F_o - |F_c||^2$), the *R* factor was 0.096 and the weighted *R* factor 0.121; the weighting scheme used was $w = 2.2525/[\sigma^2(F) + 0.002287 F^2]$. In the final cycles of refinement, the maximum shift/e.s.d. was 0.139 and the average shift/e.s.d. was 0.036. The final difference-electron-density synthesis showed maximum and minimum electron densities of 0.286 and -0.352 e.Å^{-3}, respectively.

Calculations for both compounds were performed on the Dundee University PRIME 6350 computer, using the SHEL-XS[19] and SHEL-X76[20] program systems. Atomic scattering factors were taken from the libraries in the programs. Calculations of molecular geometry were obtained using XANADU[21], and drawings were prepared using PLUTO[22]. In the numbering scheme used (see Figs. 1 and 2), the carbon and oxygen atoms of the parent sugar are numbered in the normal carbohydrate convention and the remaining atoms are numbered arbitrarily.

Observed and calculated structure-factors, anisotropic thermal vibrational parameters, and calculated positions of the hydrogen atoms for both **8** and **9** have been deposited*.

ACKNOWLEDGMENT

We thank Mr. J. Paton for assistance with the crystal-structure determinations.

REFERENCES

1 J. S. Brimacombe, G. McDonald, and M. A. Rahman, *Carbohydr. Res.*, 205 (1990) 422–427.
2 G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, 5 (1970) 167–203.
3 J. M. J. Tronchet and T. N. Xuan, *Carbohydr. Res.*, 67 (1978) 469–478.
4 J. K. Cha, W. J. Christ, and Y. Kishi, *Tetrahedron*, 40 (1984) 2247–2255.
5 M. P. Deninno, S. J. Danishefsky, and G. Schulte, *J. Am. Chem. Soc.*, 110 (1988) 3925–3929.
6 K. N. Houk, S. R. Moses, Y.-D. Wu, N. G. Rondan, Y. Jäger, R. Schohe, and F. R. Fronczek, *J. Am. Chem. Soc.*, 106 (1984) 3880–3882.
7 G. Stork and M. Kahn, *Tetrahedron Lett.*, 24 (1983) 3951–3954.
8 E. R. Larson and S. J. Danishefsky, *J. Am. Chem. Soc.*, 105 (1983) 6715–6716; S. J. Danishefsky, E. R. Larson, and J. P. Springer, *ibid.*, 107 (1985) 1274–1280.
9 J. C. Barnes, J. S. Brimacombe, and D. J. Irvine, *Carbohydr. Res.*, 200 (1990) 77–89.
10 J. S. Brimacombe and A. K. M. S. Kabir, *Carbohydr. Res.*, 179 (1988) 21–30; A. Bernardi, S. Cardani, C. Solastico, and R. Villa, *Tetrahedron*, 44 (1988) 491–502.
11 J. S. Brimacombe and A. K. M. S. Kabir, *Carbohydr. Res.*, 152 (1986) 335–338.
12 S. J. Danishefsky and M. P. Deninno, *J. Org. Chem.*, 51 (1986) 2615–2617; S. J. Danishefsky and M. P. Deninno, *Angew. Chem. Int. Ed. Engl.*, 26 (1987) 15–23.

---

* Lists of F_o and F_c structure-factors, anisotropic vibrational parameters, and calculated positions of the hydrogen atoms are deposited with, and can be obtained from, Elsevier Science Publishers, B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/468/ *Carbohydr. Res.*, 216 (1991) 11–20.

13 D. Y. Curtin and L. P. Hammett, in E. L. Eliel (Ed.), *Stereochemistry of Carbon Compounds*, McGraw-Hill, New York, 1962, pp. 237–239.

14 G. B. Howarth, D. G. Lance, W. A. Szarek, and J. K. N. Jones, *Can. J. Chem.*, 47 (1969) 75–79; R. Hems, D. Horton, and M. Nakadate, *Carbohydr. Res.*, 25 (1972) 205–216.

15 J. S. Brimacombe and A. K. M. S. Kabir, *Carbohydr. Res.*, 174 (1988) 37–45.

16 J. S. Brimacombe, R. Hanna, A. K. M. S. Kabir, F. Bennett, and I. D. Taylor, *J. Chem. Soc., Perkin Trans. 1*, (1986) 815–821.

17 E. Vedejs and C. K. McClure, *J. Am. Chem. Soc.*, 108 (1986) 1094–1096.

18 M. Schröder, *Chem. Rev.*, 80 (1980) 187–213.

19 G. M. Sheldrick, *SHEL-XS Program for Crystal Structure Determination*, University of Göttingen, 1986.

20 G. M. Sheldrick, *SHEL-X76 Program for Crystal Structure Determination*, University of Cambridge, 1975.

21 P. Roberts and G. M. Sheldrick, *XANADU Program for Molecular Geometry Calculations*, University of Cambridge, 1975.

22 W. D. S. Motherwell and W. Clegg, *PLUTO Program for Plotting Molecular and Crystal Structures*, University of Cambridge, 1978.