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The effect of double-bond geometry on the crystallographic conformations of two enopyranuronates*

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ABSTRACT

In the crystal structure of methyl (*Z*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranuronate (**10**), the allylic system adopts an eclipsed conformation with the smallest group, H-7, at the adjacent stereocentre eclipsing the olefinic double bond. The allylic system of methyl (*E*)-6-*O*-benzyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-non-7-enopyranuronate (**11**) also adopts an eclipsed conformation in the crystal, but with the benzyloxy group at the adjacent stereocentre eclipsing the olefinic double bond. These ground-state conformations in the solid state provide some insight into the vastly different facial stereoselectivities of **10** and **11** towards catalytic osmylation.

INTRODUCTION

The vicinal *syn*-hydroxylation of olefins with OsO_4 is among the most selective and reliable of organic reactions[1]. The introduction of catalytic processes[2] to offset the expense and toxicity of OsO_4 has substantially increased the practicality and attractiveness of such transformations, notably in the synthesis of higher-carbon sugars[3–8]. In ascending the sugar series, it is essential to know as much as possible about the stereoselectivities of the reactions used, especially when the reaction pathway is not well defined, as is the case with osmylations[1,9]. Several of the models used to predict the stereochemical outcome of the osmylation of chiral allylic systems are based on reactant-like transition states[10–12] that require some knowledge of the ground-state conformation of the unsaturated substrate. Valuable information about the ground-state conformation can be obtained by X-ray crystallography, and it is instructive to compare the crystallographic ground-state conformations of allylic systems with those used in various models. Indeed, a strong correlation between the crystallographic ground-state conformations of several alkenylpyranosides and the stereochemical outcome of their reactions with OsO_4 has already been revealed[12].

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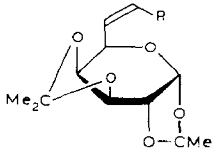
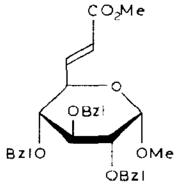
RESULTS AND DISCUSSION

Before looking at the crystal structures, it would be appropriate to discuss briefly the current position with regard to the osmylation of allylic systems. From an examination of the stereochemical outcome of the osmylation of a series of chiral allylic alcohols, Kishi and his co-workers[10] concluded that the hydroxyl or alkoxyl group at the adjacent stereocentre had an important role in determining the degree of stereoselectivity. This conclusion led them to the empirical formulation that, in the osmylation of chiral allylic alcohols, the relative stereochemistry between the pre-existing hydroxyl or alkoxyl group and the newly introduced hydroxyl group of the major product is *erythro*[10]. Osmylations of many chiral allylic alcohols (for example, **1**[4]) conform to Kishi's empirical rule to a greater or lesser degree[4-6,10]. It is also evident that, whereas osmylations of (*E*)-conjugate esters (for example, **2**[13]) conform to Kishi's empirical rule and often exhibit high stereoselectivities[6,11-14], most of the exceptions are to be found[4,6,10,12,14] among those involving (*Z*)-conjugate esters (for example, **3**[4]). There seems to be a rough division between simple electron-rich allylic systems[6,10], for which the (*Z*)-isomers usually show higher facial selectivity than the corresponding (*E*)-isomers, and those systems having the olefinic double bond in conjugation with an electron-withdrawing group[4,6,10,12,14], for which the (*Z*)-isomers, unlike the corresponding (*E*)-isomers, may exhibit low facial selectivity or breach Kishi's rule.



1 R = CH$_2$OH
3 R = CO$_2$Me



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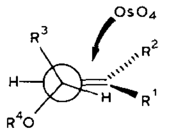
Based on the known preference for allylic systems to adopt an eclipsed conformation[15,16], and assuming that this preference persists in the transition state, Kishi and his co-workers[10] suggested that the stereochemical outcome of the osmylation process might result from preferential attack of OsO$_4$ on the face of the olefinic double bond opposite to that of the pre-existing hydroxyl (or alkoxyl) group when the molecule adopts the sterically least-compressed conformation **4** (*cf.* the other eclipsed conformations **5** and **6**). The fact that the stereoselectivity observed in the osmylation of (*Z*)-allylic alcohols and their derivatives, for which the eclipsed conformation **4** (R^1 = alkyl of CH$_2$OH, R^2 = H) would be expected to be most prevalent, is usually higher than that or the corresponding (*E*)-isomers was cited[10] in support of this mode of attack. X-Ray crystallographic analysis has shown[12] that the C-5–H bond does indeed eclipse the olefinic double bond in the ground-state conformation of the (*E*)-heptenopyranoside derivative **7**, which undergoes a highly stereoselective osmylation[7] in conformity with Kishi's empirical rule[10].



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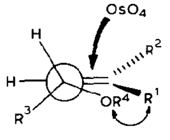

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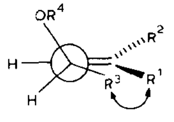

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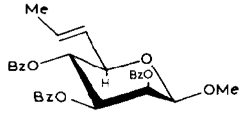
When taken together, the results obtained for the osmylation of (*E*)- and (*Z*)-conjugate esters do not fit comfortably with the model **4** proposed by Kishi[10]. As indicated earlier, most of the exceptions to Kishi's empirical rule and some of the lowest stereoselectivities occur among osmylations of (*Z*)-conjugate esters[4,6,10,14], which, for steric reasons, should exhibit a strong preference for the conformation **4** (R^1 = CO_2alkyl, R^2 = H) in which the smallest group at the adjacent stereocentre eclipses the olefinic double bond. Should this conformation be adopted by (*Z*)-conjugate esters, attack of OsO_4 on the olefinic double bond must occur *syn*, rather than *anti*[10], to the allylic oxygen atom at the adjacent stereocentre when Kishi's empirical rule is breached. Regarding this, it is pertinent to note that the (*Z*)-conjugate ester **8** adopts an anti-periplanar arrangement of the allylic C–O and olefinic bonds in the solid state[12], and undergoes stereospecific *syn*-hydroxylation with OsO_4 from the less hindered α-face to give[8] the anti-Kishi product. Presumably, if non-bonded interactions become too severe, (*Z*)-conjugate esters may forgo the usual advantages[15] of an eclipsed conformation about the allylic system and adopt a staggered form. This situation contrasts with the virtual eclipsing of the allylic C–O and olefinic bonds found[12] in the crystal structure of the (*E*)-isomer **9** of **8**. This synplanar (or "alkoxy-inside"[17]) conformation, akin to **5** (R^1 = H, R^2 = CO_2Me), allows easy access to the olefinic double bond from the α-face, yielding[12] principally the product predicted by Kishi's empirical rule on osmylation of **9**. An "alkoxy-inside" model was invoked originally by Stork and Kahn[11] in rationalising the facial stereoselectivities of a series of (*E*)-conjugate esters; its advantage is that it avoids a destabilizing overlap, present in the least compressed conformation **4**, between the electron-withdrawing allylic C–O bond and the already electron-deficient π-system[12,17]. Danishefsky and his co-workers[12] also concluded that the stereochemical outcome of such osmylations are best accommodated by the ground-state conformation in which the olefinic double bond is maximally nucleophilic[17]. However, the crucial electronic role of allylic substituents in determining the preferred transition-state conformation has been questioned, and a model more "product-like" than Kishi's, which considers primarily the steric interactions of the incoming electrophile and the allylic system, has been proposed[18].



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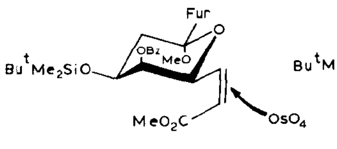

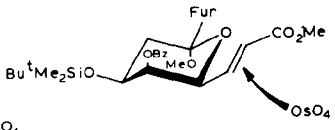

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8 Fur = furan-2-yl

Despite the theoretical limitations[19] imposed by using the ground-state conformation to predict the stereochemical outcome of reactions, there is a strong correlation between the crystallographic ground-state conformations of the (*Z*)- and (*E*)-conjugate esters **8** and **9**, respectively, and their facial stereoselectivities towards osmylation[12]. During the course of our own studies, the *αβ*-unsaturated pyranuronates **10**[20] and **11**[21] were found to exhibit widely different selectivities in their reactions with OsO_4. Methyl (*Z*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-*α*-D-*threo*-D-*galacto*-dec-8-enopyranuronate (**10**) exhibited[20] virtually no facial stereoselectivity towards osmylation, whereas methyl (*E*)-6-*O*-benzyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-*α*-D-*glycero*-D-*galacto*-non-7-enopyranuronate (**11**) yielded[21] the predicted (Kishi[10]) product with exceptionally high facial stereoselectivity (ratio of diastereoisomers ~17:1).

The X-ray structure of the (*Z*)-decenopyranuronate derivative **10**[20] (see Experimental section for crystal data and other information) is shown in Fig. 1, 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 **10** are visible in Fig. 1, which shows that the allylic system adopts an eclipsed conformation akin to **4** (R^1 = CO_2Me, R^2 = H) with the smallest group, H-7, eclipsing the olefinic double bond (H-7–C-7–

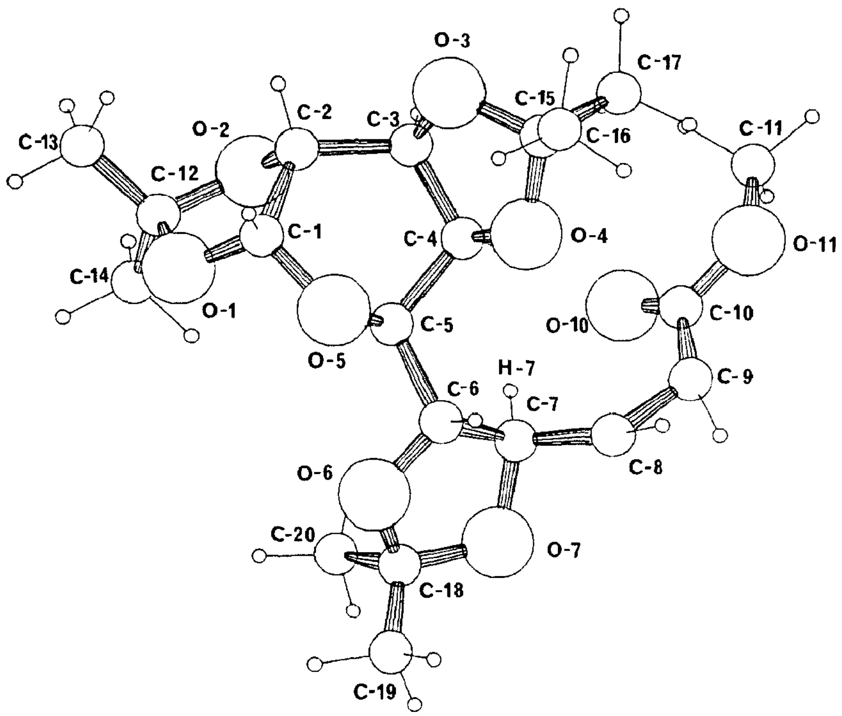
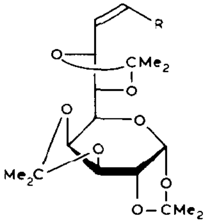
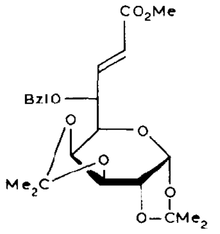


Fig. 1. Stereoview of methyl (*Z*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-*α*-D-*threo*-D-*galacto*-dec-8-enopyranuronate (**10**), and the numbering scheme used.



10 R = CO_2Me
13 R = CH_2OH



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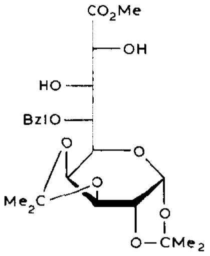

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TABLE I

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

Atom	x/a	y/b	z/c	U*eq*
C-1	508(14)	3655(6)	−2681(20)	78(6)
C-2	−559(12)	3214(5)	−2588(14)	60(4)
C-3	−449(12)	2706(5)	−1315(14)	64(5)
C-4	315(11)	2834(5)	40(16)	66(5)
C-5	760(11)	3488(5)	47(18)	62(5)
C-6	1714(12)	3628(5)	1258(15)	64(5)
C-7	1327(12)	3436(4)	2811(11)	43(4)
C-8	2002(12)	2931(5)	3351(13)	68(5)
C-9	1555(13)	2392(6)	3887(17)	86(6)
C-10	283(15)	2227(5)	3819(20)	102(6)
C-11	−980(19)	1394(7)	3760(31)	188(13)
C-12	−1286(16)	4168(7)	−2674(22)	95(7)
C-13	−1790(15)	4224(6)	−4164(23)	127(8)
C-14	−1769(15)	4631(6)	−1538(18)	118(7)
C-15	994(13)	1966(5)	−1077(12)	58(5)
C-16	2079(13)	1750(7)	−1916(19)	106(6)
C-17	338(15)	1501(5)	−174(17)	86(6)
C-18	1897(19)	4442(6)	2686(19)	98(7)
C-19	2803(24)	4797(9)	3080(20)	241(17)
C-20	668(22)	4781(10)	2812(37)	251(18)
O-1	−26(10)	4209(4)	−2740(12)	92(4)
O-2	−1497(8)	3594(4)	−1977(10)	74(3)
O-3	180(8)	2239(3)	−2165(9)	76(3)
O-4	1315(8)	2446(4)	−103(11)	81(3)
O-5	1302(8)	3614(4)	−1370(12)	65(3)
O-6	1901(10)	4228(4)	1320(11)	99(4)
O-7	1733(8)	3939(4)	3737(10)	82(3)
O-10	−584(9)	2551(4)	3854(12)	103(3)
O-11	163(14)	1644(4)	3777(15)	142(6)

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

TABLE II

Bond lengths (Å) for **10**

Bond		*Bond*	
C-1–C-2	1.555(20)	C-9–C-10	1.470(22)
C-1–O-1	1.388(17)	C-10–O-10	1.216(18)
C-1–O-5	1.440(19)	C-10–O-11	1.324(15)
C-2–C-3	1.594(17)	C-11–O-11	1.397(25)
C-2–O-2	1.453(15)	C-12–C-13	1.409(27)
C-3–C-4	1.476(19)	C-12–C-14	1.531(23)
C-3–O-3	1.464(15)	C-12–O-1	1.412(21)
C-4–C-5	1.560(16)	C-12–O-2	1.449(19)
C-4–O-4	1.426(15)	C-15–C-16	1.494(20)
C-5–C-6	1.525(19)	C-15–C-17	1.498(18)
C-5–O-5	1.394(18)	C-15–O-3	1.446(15)
C-6–C-7	1.473(16)	C-15–O-4	1.418(14)
C-6–O-6	1.372(14)	C-18–C-19	1.335(31)
C-7–C-8	1.445(17)	C-18–C-20	1.575(31)
C-7–O-7	1.460(13)	C-18–O-6	1.275(19)
C-8–C-9	1.396(19)	C-18–O-7	1.467(17)

C-8–C-9 −1.9°). The C=C–C=O segment adopts an *s-cis* geometry that is somewhat distorted from coplanarity (C-8–C-9–C-10–O-10 −28.8°). The eclipsed conformation having the smallest group eclipsing the olefinic double bond would be favoured on steric grounds. It also appears that, in this conformation, the approach of a large electrophile like OsO_4 to the olefinic double bond would be restricted to some extent in the direction *anti* to the allylic oxygen atom at C-7 (Kishi model[10]) by the overhanging 3,4-*O*-isopropylidene group (see Fig. 1). If this direction of attack is preferred[10], then partial shielding on this side would account for the virtual absence of facial stereoselectivity on osmylation of **10** and, equally, the corresponding (*Z*)-decenopyranose derivative **13**[6], which would be expected to adopt a similar conformation. The osmylation of **10** contrasts sharply with that of the (*Z*)-conjugate ester **8**, which undergoes a virtually stereospecific *syn*-hydroxylation in an anti-Kishi sense[8], most likely in the antiperiplanar conformation shown[12].

The X-ray structure of the (*E*)-nonenopyranuronate **11**[21] (see Experimental section for crystal data and other information) is shown in Fig. 2, 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 IV.

Inspection of Fig. 2 reveals that the C-6–O-6 bond eclipses the olefinic double bond (O-6–C-6–C-7–C-8 5.65°) in an "alkoxy-inside" conformation, and that the C=C–C=O segment adopts an *s-trans* geometry (C-7–C-8–C-9–O-9 180.0°) with perfect coplanarity. The major diastereoisomer **12** produced[21] on osmylation of **11** is the one conforming to Kishi's empirical rule[10] and, for the conformation shown in Fig. 2, would result from attack of OsO_4 on the olefinic double bond from the same side as H-6, the smallest of the groups at the adjacent stereocentre. The "alkoxy-inside" conforma-

TABLE III

Bond angles and selected torsion angles (degrees) for **10**

Bond angles			
C-2–C-1–O-1	104.4(12)	C-13–C-12–C-14	112.5(14)
C-2–C-1–O-5	113.0(12)	C-13–C-12–O-1	110.8(15)
O-1–C-1–O-5	110.6(12)	C-13–C-12–O-2	113.2(13)
C-1–C-2–C-3	115.9(11)	C-14–C-12–O-1	109.5(13)
C-1–C-2–O-2	101.2(9)	C-14–C-12–O-2	106.7(13)
C-3–C-2–O-2	103.4(9)	O-1–C-12–O-2	103.7(12)
C-2–C-3–C-4	116.7(10)	C-16–C-15–C-17	114.9(11)
C-2–C-3–O-3	102.2(9)	C-16–C-15–O-3	109.6(10)
C-4–C-3–O-3	105.2(10)	C-16–C-15–O-4	109.3(11)
C-3–C-4–C-5	111.9(10)	C-17–C-15–O-3	109.2(11)
C-3–C-4–O-4	105.3(10)	C-17–C-15–O-4	110.5(9)
C-5–C-4–O-4	109.4(10)	O-3–C-15–O-4	102.6(9)
C-4–C-5–C-6	114.9(11)	C-19–C-18–C-20	110.7(16)
C-4–C-5–O-5	109.2(11)	C-19–C-18–O-6	117.4(17)
C-6–C-5–O-5	104.8(10)	C-19–C-18–O-7	113.7(15)
C-5–C-6–C-7	111.0(11)	C-20–C-18–O-6	104.6(17)
C-5–C-6–O-6	109.7(10)	C-20–C-18–O-7	103.0(16)
C-7–C-6–O-6	107.4(10)	O-6–C-18–O-7	106.1(11)
C-6–C-7–C-8	111.9(10)	C-1–O-1–C-12	111.6(11)
C-6–C-7–O-7	100.3(9)	C-2–O-2–C-12	105.1(10)
C-8–C-7–O-7	105.9(10)	C-3–O-3–C-15	106.5(8)
C-7–C-8–C-9	127.5(12)	C-4–O-4–C-15	108.9(10)
C-8–C-9–C-10	123.6(12)	C-1–O-5–C-5	115.7(10)
C-9–C-10–O-10	128.1(12)	C-6–O-6–C-18	114.3(11)
C-9–C-10–O-11	110.5(13)	C-7–O-7–C-18	107.6(9)
O-10–C-10–O-11	121.3(15)	C-10–O-11–C-11	119.6(14)
Torsion angles			
C-6–C-7–C-8–C-9	−126.3	H-7–C-7–C-8–C-9	−1.9
O-7–C-7–C-8–C-9	+125.3	C-8–C-9–C-10–O-10	−28.8

tion is also the preferred crystallographic ground-state conformation of the (*E*)-conjugate ester **9**[12], and seems to be particularly favoured *in solution* by (*E*)-allylic systems having groups that withdraw electrons by resonance attached to the olefinic double bond[16,22]. Not only does the "alkoxy-inside" conformation reduce electron depletion of the π-system, but it also places the best σ-donor *anti* to the incoming electrophile in the transition state of electrophilic additions[23]. The view has been expressed that the preference for allylic systems (such as **9** and **11**) to adopt the "alkoxy-inside" conformation for electrophilic additions should hold generally, unless it is disfavoured by bulky electrophiles or *cis*-substituents on the olefinic double bond[17]. Since both of these qualifications apply to the osmylation of (*Z*)-allylic systems, the uncertainties of predictions based on this model are sharply increased in these cases. On the other hand, qualitative predictions of the stereochemical outcome of the osmylation of (*E*)-conjugate esters based on this model are correct and coincide with those obtained using Kishi's model.

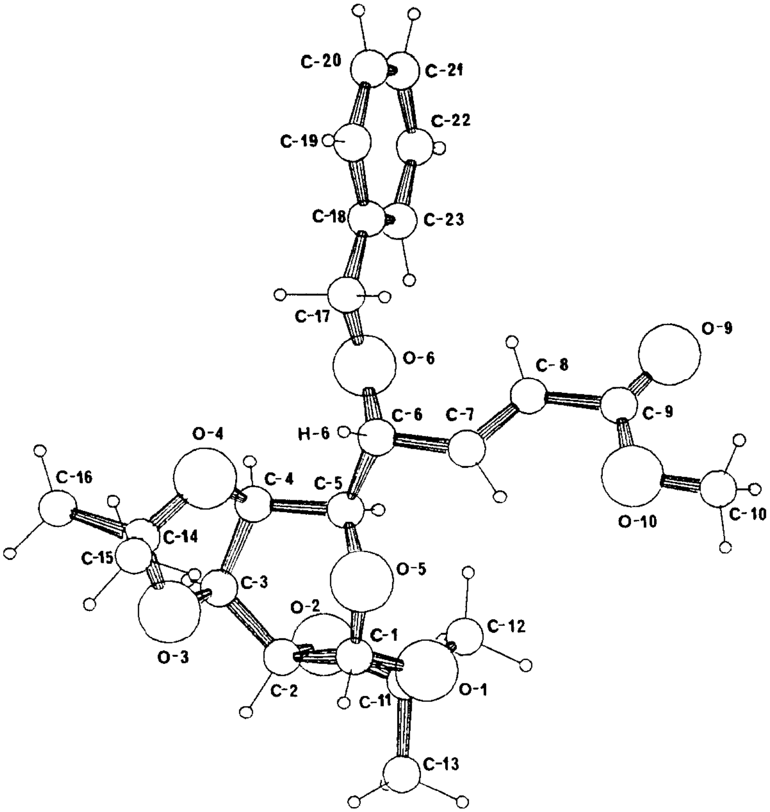

Fig. 2. Stereoview of methyl (*E*)-6-*O*-benzyl-7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-non-7-enopyranuronate (**11**), and the numbering scheme used.

Although we have previously argued[13] in favour of retaining the Kishi model **4** to predict the stereochemical outcome of osmylations involving chiral allylic systems, theoretical[16,17,23] and experimental[12,16] evidence, including the results obtained herein, persuade us to modify this stance in favour of the "alkoxy-inside" model **5** (R^1 = H, R^2 = $\mathrm{CO_2}$alkyl) for osmylations involving (*E*)-conjugate esters, although both models lead to identical qualitative predictions. Significantly, the "alkoxy-inside" conformation is revealed as the crystallographic ground-state conformation of the (*E*)-conjugate esters **9**[12] and **11**, both of which can use this conformation to undergo highly stereoselective osmylations from the less hindered face of the olefinic double bond. While steric factors militate against the "alkoxy-inside" conformation **5** (R^1 = $\mathrm{CO_2}$alkyl, R^2 = H) for (*Z*)-conjugate esters, no clear candidate for the preferred ground-state conformation about the allylic system has emerged. Where crystallographic evidence has been obtained, it is divided between the least-compressed eclipsed conformation favoured by Kishi's model[10] for **10** (this paper) and the antiperiplanar conformation for **8**[12]. Although current models[10–12,17,18] can often provide explanations for the vagaries encoun-

TABLE IV

Fractional co-ordinates (× 10^4)^a and equivalent isotropic temperature factors (× 10^3)^b for **11**

Atom	x/a	y/b	z/c	*Ueq*
C-1	−259(8)	−2948(4)	2853(10)	41(2)
C-2	695(10)	3411(3)	2404(10)	50(3)
C-3	712(9)	−3531(4)	812(10)	52(3)
C-4	555(9)	−2991(3)	−180(10)	46(3)
C-5	123(9)	−2447(4)	649(10)	49(3)
C-6	−513(8)	−1961(3)	−300(10)	47(3)
C-7	−920(9)	−1453(3)	611(9)	49(3)
C-8	−561(9)	−876(4)	439(12)	56(3)
C-9	−1004(10)	−355(4)	1317(12)	57(3)
C-10	−2154(15)	−45(5)	3269(15)	114(6)
C-11	1578(11)	−2775(4)	4057(11)	60(3)
C-12	2436(12)	−2263(4)	4090(12)	78(4)
C-13	1596(17)	−3157(6)	5425(12)	115(6)
C-14	−712(9)	−3779(4)	−943(10)	50(3)
C-15	−2072(11)	−3865(5)	−999(12)	74(4)
C-16	−14(12)	−4191(4)	−1994(13)	79(4)
C-17	−131(9)	−1598(4)	−2670(10)	55(3)
C-18	747(6)	−1201(3)	−3453(7)	53(3)
C-19	372(6)	−990(3)	−4798(7)	74(4)
C-20	1162(6)	−622(3)	−5598(7)	87(5)
C-21	2327(6)	−464(3)	−5053(7)	70(4)
C-22	2702(6)	−676(3)	−3708(7)	68(4)
C-23	1912(6)	−1044(3)	−2908(7)	67(4)
O-1	318(7)	−2579(3)	3835(7)	69(2)
O-2	1816(6)	−3134(2)	2817(7)	53(2)
O-3	−297(7)	−3906(2)	516(7)	58(2)
O-4	−369(8)	−3166(3)	−1192(7)	67(2)
O-5	−752(6)	−2608(2)	1701(6)	51(2)
O-6	413(5)	−1778(2)	−1316(7)	49(2)
O-9	−634(9)	146(3)	1080(9)	91(3)
O-10	−1759(7)	−529(3)	2366(9)	81(3)

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

tered on osmylation of chiral (*Z*)-conjugate esters, they are less effective in a predictive mode.

EXPERIMENTAL

Crystal data for **10**[12]. — $C_{20}H_{30}O_9$; M = 414.45; orthorhombic, space group $P2_12_12_1$; a = 11.174(8), b = 22.584(18), c = 8.63(3) Å; volume = 2177.81 Å^3, D_c = 1.26 g.cm^{-3}, Z = 4, F(000) = 888, λ (Mo-K_α) = 0.71069 Å, μ = 0.62 cm^{-1}.

Crystal data for **11**[21]. — $C_{23}H_{30}O_8$; M = 434.49; orthorhombic, space group $P2_12_12_1$; a = 10.747(5), b = 22.254(12), c = 9.294(6) Å; volume = 2222.79 Å^3, D_c = 1.30 g.cm^{-3}, Z = 4, F(000) = 928, λ (Mo-K_α) = 0.71069 Å, μ = 0.59 cm^{-1}.

Data collection. — Data for both compounds were collected using a Stoe Stadi II

TABLE V

Bond lengths (Å) for **11**

Bond		*Bond*	
C-1–C-2	1.511(13)	C-10–O-10	1.431(15)
C-1–O-1	1.376(11)	C-11–C-12	1.465(15)
C-1–O-5	1.415(11)	C-11–C-13	1.529(15)
C-2–C-3	1.504(13)	C-11–O-1	1.437(13)
C-2–O-2	1.406(12)	C-11–O-2	1.426(12)
C-3–C-4	1.525(12)	C-14–C-15	1.475(15)
C-3–O-3	1.395(12)	C-14–C-16	1.535(15)
C-4–C-5	1.508(12)	C-14–O-3	1.455(12)
C-4–O-4	1.422(12)	C-14–O-4	1.433(10)
C-5–C-6	1.554(12)	C-17–C-18	1.483(11)
C-5–O-5	1.403(11)	C-17–O-6	1.443(11)
C-6–C-7	1.479(12)	C-18–C-19	1.395(9)
C-6–O-6	1.431(11)	C-18–C-23	1.395(9)
C-7–C-8	1.350(11)	C-19–C-20	1.395(9)
C-8–C-9	1.495(14)	C-20–C-21	1.395(9)
C-9–O-9	1.204(12)	C-21–C-22	1.395(9)
C-9–O-10	1.326(14)	C-22–C-23	1.395(9)

diffractometer. 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 refined in groups.

Structure analysis for **10** (Tables I–III). — Cell dimensions were refined from 12 carefully centred reflections ($12 \leqslant \theta \leqslant 16°$) with a crystal measuring approximately 0.58 × 0.22 × 0.22 mm mounted along the *c* (needle) axis. Data were collected over the range $2 \leqslant 2\theta \leqslant 50°$. From the 1956 reflections measured, 1418 unique data (R_{int} = 0.062) were obtained; 918 reflections with $F \geqslant 4\sigma(F)$ were used in further refinements. Range of indices: $-1 \leqslant h \leqslant 12$, $-1 \leqslant k \leqslant 24$, $0 \leqslant l \leqslant 7$. After refinement (265 parameters and minimizing $\sum w|F_o - |F_c||^2$), the R factor was 0.086 and the weighted R factor was 0.098; the weighting scheme used was $w = 1.000/[\sigma^2(F) + 0.001163\,F^2]$. In the final cycles of refinement, the maximum shift/e.s.d. was 0.151 and the average shift/e.s.d. was 0.056. The final difference-electron-density synthesis showed maximum and minimum electron densities of 0.30 and −0.26 e.Å^{-3}, respectively.

Structure analysis for **11** (Tables IV–VI). — Cell dimensions were refined from 11 carefully centred reflections ($10 \leqslant \theta \leqslant 14°$) with a crystal measuring approximately 0.47 × 0.11 × 0.25 mm mounted along the *a* (needle) axis. Data were collected over the range $2 \leqslant 2\theta \leqslant 50°$. From the 2226 reflections measured, 1850 unique data (R_{int} = 0.071) were obtained; 1437 reflections with $F \geqslant 4\,\sigma(F)$ were used in further refinements. Range of indices $0 \leqslant h \leqslant 9$, $-2 \leqslant k \leqslant 26$, $-2 \leqslant l \leqslant 11$. The data were corrected for absorption using the routine in the SHEL-X76[25] program; the maximum and minimum

TABLE VI

Bond angles and selected torsion angles (degrees) for **11**

Bond angles			
C-2-C-1-O-1	106.5(7)	C-13-C-11-O-1	107.4(10)
C-2-C-1-O-5	114.2(7)	C-13-C-11-O-2	111.0(8)
O-1-C-1-O-5	110.6(7)	O-1-C-11-O-2	102.9(8)
C-1-C-2-C-3	113.7(8)	C-15-C-14-C-16	112.6(9)
C-1-C-2-O-2	102.0(6)	C-15-C-14-O-3	108.1(8)
C-3-C-2-O-2	109.6(8)	C-15-C-14-O-4	111.9(8)
C-2-C-3-C-4	116.9(7)	C-16-C-14-O-3	109.1(8)
C-2-C-3-O-3	106.9(8)	C-16-C-14-O-4	109.9(8)
C-4-C-3-O-3	105.4(8)	O-3-C-14-O-4	104.8(7)
C-3-C-4-C-5	111.0(7)	C-18-C-17-O-6	109.6(7)
C-3-C-4-O-4	105.1(6)	C-17-C-18-C-19	117.2(6)
C-5-C-4-O-4	110.0(8)	C-17-C-18-C-23	122.8(6)
C-4-C-5-C-6	113.8(7)	C-19-C-18-C-23	120.0(6)
C-4-C-5-O-5	111.0(7)	C-18-C-19-C-20	120.0(6)
C-6-C-5-O-5	106.2(7)	C-19-C-20-C-21	120.0(6)
C-5-C-6-C-7	109.7(7)	C-20-C-21-C-22	120.0(6)
C-5-C-6-O-6	105.5(7)	C-21-C-22-C-23	120.0(6)
C-7-C-6-O-6	111.5(7)	C-18-C-23-C-22	120.0(6)
C-6-C-7-C-8	125.1(9)	C-1-O-1-C-11	109.8(7)
C-7-C-8-C-9	125.5(9)	C-2-O-2-C-11	108.2(7)
C-8-C-9-O-9	120.8(10)	C-3-O-3-C-14	107.8(7)
C-8-C-9-O-10	111.7(8)	C-4-O-4-C-14	109.5(7)
O-9-C-9-O-10	127.4(10)	C-1-O-5-C-5	114.4(7)
C-12-C-11-C-13	114.0(10)	C-6-O-6-C-17	111.9(7)
C-12-C-11-O-1	111.2(8)	C-9-O-10-C-10	113.1(8)
C-12-C11-O-2	109.8(9)		
Torsion angles			
C-5-C-6-C-7-C-8	122.2	H-6-C-6-C-7-C-8	−115.6
O-6-C-6-C-7-C-8	5.65	C-7-C-8-C-9-O-9	180.0

transmission factors were 0.999 and 0.985, respectively. After final refinement (278 parameters and minimizing $\sum w|F_o - |F_c||^2$), the R factor was 0.085 and the weighted R factor 0.112; the weighting scheme used was $w = 1.000/[\sigma^2(F) + 0.001817\ F^2]$. In the final cycles of refinement, the maximum shift/e.s.d. was 0.128 (ignoring oscillating temperature parameters for the hydrogen atoms) and the average shift/e.s.d. was 0.038. The final difference-electron-density synthesis showed maximum and minimum electron densities of 0.34 and −0.37 e.Å^{-3}, respectively.

Calculations for both compounds were performed on the Dundee University PRIME 6350 computer, using the SHEL-XS[24] and SHEL-X76[25] program systems. Atomic scattering factors were taken from the libraries in the programs. Calculations of molecular geometry were obtained using XANADU[26] and drawings were prepared using PLUTO[27]. 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 **10** and **11** have been deposited*.

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*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/433 *Carbohydr. Res.*, 200 (1990) 77–89.

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