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Methyl 2,4-Dideoxy-6,7,8,9,10-penta-*O*-acetyl-D-*glycero*-α-D-*gluco*-decapyranosid-3-ulose

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Abstract. $C_{21}H_{30}O_{13}$, $M_r = 490.46$, orthorhombic, $P2_12_12_1$, $a = 8.945$ (2), $b = 22.104$ (6), $c = 12.482$ (4) Å, $V = 2468$ (1) Å^3, $Z = 4$, $D_x = 1.320$ (1) Mg m^{-3}, λ(Cu Kα) = 1.5418 Å, $\mu = 0.96$ mm^{-1}, $F(000) = 1040$, room temperature, $R = 0.072$ for 1554 independent reflections with $I > 2\sigma(I)$. The pyranoid ring has the almost ideal $^4C_1$ chair conformation and is more puckered than analogous rings with the C(sp^2) atom vicinal to the anomeric centre. The aliphatic chain has an extended *ap*, *ap* conformation.

Introduction. Recently we have studied the crystal structures and conformations of several pyranosides with one sp^2-hybridized C atom in position 2 (vicinal to the anomeric centre) of the pyranoid ring (Smiatacz, Myszka & Ciunik, 1988; Ciunik, Paulsen, Luger, Smiatacz & Myszka, 1989; Ciunik, Szweda & Smiatacz, 1991). All these compounds have a chair conformation with a large distortion towards an envelope geometry or a small one towards a half chair. These pyranoid rings are more distorted and probably more flexible than the parent compounds with all C atoms sp^3 hybridized. The second conclusion is supported by observed differences between conformations of similar 2-oxyimino derivatives of pyranosides studied and between symmetry-independent molecules in two crystal structures. An inspection of carbohydrate derivatives with the C(sp^2) atom in position 3 of the pyranoid ring, *i.e.*

opposite to the acetal O atom (Arnoux, Pascard, Raynaud & Lunel, 1980; Bednarski & Danishefsky, 1986), shows that these chair rings are generally less distorted than compounds with the $C(sp^2)$ atom in position 2 of the ring. Because the former group of compounds is rather a small one we decided to solve the crystal structure of the title compound (I) and thus enable further comparisons.

(I)
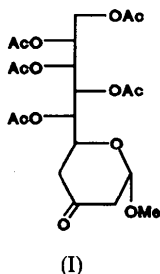
Experimental. For the synthesis of the target compound, penta-O-acetyl-aldehydo-D-glucose was prepared according to a previously published method (Wolfrom & Thomson, 1963). Danishefsky's diene (trans,trans-1-methoxy-3-trimethylsilyloxy-1,3-butadiene) is a commercially available substance (Aldrich).

Preparation of 1,5-anhydro-2,4-dideoxy-6,7,8,9,10-penta-O-acetyl-D-glycero-D-gluco-dec-1-en-3-ulose (1). To a solution of 2.8 g (7.18 mmol) penta-O-acetyl-aldehydo-D-glucose and 1.4 ml (1.24 g; 7.20 mmol) Danishefsky's diene in 50 ml toluene and 0.5 ml dichloromethane cooled on ice, 100 mg anhydrous zinc chloride was added. After stirring overnight at room temperature, the solution was decanted and evaporated to dryness. The residue was purified by column chromatography (silica gel 60, 0.063–0.200 mm, Merck, Darmstadt, Germany) using diethyl ether as solvent. Crystallization from diethyl ether/light petroleum yielded 1.7 g (52%) of (1); m.p. 369 K; $[\alpha]_D^{20°C} = 98.9$ ($c \neq 0.5$, CHCl_3). Analysis: calculated for $C_{20}H_{26}O_{12}$ ($M_r = 458.42$) C 52.40, H 5.72%; found C 52.26, H 5.79%.

Preparation of methyl 2,4-dideoxy-6,7,8,9,10-penta-O-acetyl-D-glycero-α-D-gluco-decapyranosid-3-ulose (2). To a solution of 1.12 g (2.44 mmol) (1) in 22 ml dry methanol, about ten pearls of 4 Å molecular sieve and 0.1 ml triethylamine were added. The mixture was stirred overnight, filtered, and evaporated to dryness. The residue was purified by HPLC (silica gel; diethyl ether). Crystallization from methanol/diethyl ether/light petroleum afforded 0.7 g (58%) of (2): m.p. 358 K; $[\alpha]_D^{20°C} = 66.6$ ($c \neq 0.5$, CH_3OH). Analysis: calculated for $C_{21}H_{30}O_{13}$ ($M_r = 490.46$) C 51.43, H 6.17%; found C 51.39, H 6.28%.

Structure determination. A crystal of dimensions $0.5 \times 0.3 \times 0.04$ mm was used for data collection on a DEC micro-PDP11-controlled Stoe-AED diffractometer, with Ni-filtered Cu $K\alpha$ radiation. Lattice parameters were determined from 30 reflections (30 $\leq 2\theta \leq 40°$). Using $\omega/2\theta$ scans, data were collected for $5 \leq 2\theta \leq 127°$, $0 \leq h \leq 10$, $0 \leq k \leq 25$, $0 \leq l \leq 14$. Two standard reflections showed no variation. Of a total of 2358 reflections collected [$0.0425 \leq (\sin\theta)/\lambda \leq 0.5815$ Å^{-1}], all independent, 1554 with $I > 2\sigma(I)$ were considered observed. No absorption correction was applied. The structure was solved by direct methods and refined (on F) with anisotropic temperature factors by the least-squares full-matrix method. Some of the H-atom positions were calculated based on the geometry of the molecule (C—H $= 0.95$ Å); the remaining H atoms were found in ΔF syntheses. In the last stage of refinement of the structure, the default value of the isotropic extinction correction (Zachariasen, 1963, 1967), $g = 0.03$, was included. Refinement of all 307 non-H-atom parameters converged with $R = 0.072$, $wR = 0.067$ [$w = \sigma^{-2}(F)$] and $S = 1.788$; final $(\Delta/\sigma)_{max} \leq 0.09$; $-0.44 \leq \Delta\rho \leq 0.42$ e Å^{-3}. The final atomic parameters are given in Table 1.* All crystallographic computations were performed using *SHELXS*90 (Sheldrick, 1990), *XTAL*2.2 (Hall & Stewart, 1987) (with neutral-atom scattering factors and anomalous-dispersion corrections as included in the program), the *XTAL* version of *ORTEP*II (Johnson, 1971), and *PUCK*2 (Luger & Bülow, 1983).

Discussion. The numbering scheme and overall conformation of the title compound are shown in Fig. 1. Selected bond distances, valency angles and dihedral angles are listed in Table 2.

The pyranoid ring has the chair conformation. The Cremer & Pople (1975) ring-puckering parameters, $Q = 0.51$ (1) Å, $\theta = 6$ (1) and $\varphi = 70$ (14)°, indicate the $^4C_1$ chair geometry (Jeffrey & Yates, 1979). The value of the θ parameter, which characterizes distortion of the chair conformation (for an ideal $^4C_1$ chair conformation $\theta = 0°$), is close to values observed in pyranosides with all C atoms in the ring sp^3 hybridized. Compounds with the $C(sp^2)$ atom in the vicinal position to the anomeric centre of the pyranoid ring are more distorted than the compound studied and have θ parameters between 6.9 and 26.5°.

The aliphatic chain C(6)—C(7)—C(8)—C(9)—C(10), equatorially substituted to the ring, has the extended *ap*, *ap* conformation with the vicinal OAc

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters ($\mathring{A}^2 \times 10^2$) for non-H atoms*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	−0.393 (1)	0.7528 (4)	0.2020 (7)	7.9 (3)
O(3)	−0.4003 (9)	0.7921 (4)	0.4666 (6)	8.5 (4)
O(5)	−0.1344 (9)	0.7533 (3)	0.2218 (6)	6.8 (3)
O(6)	0.1298 (7)	0.7986 (3)	0.2952 (5)	4.6 (2)
O(61)	0.218 (1)	0.7591 (5)	0.1424 (6)	10.3 (4)
O(7)	0.2153 (7)	0.9097 (3)	0.2487 (5)	5.1 (2)
O(71)	0.2632 (9)	0.9180 (4)	0.4248 (6)	8.3 (3)
O(8)	−0.0264 (8)	0.9309 (3)	0.0908 (5)	5.3 (2)
O(81)	−0.2751 (9)	0.9163 (4)	0.0900 (6)	6.8 (3)
O(9)	0.0335 (8)	1.0286 (3)	0.3160 (5)	5.3 (2)
O(91)	0.2653 (9)	1.0684 (4)	0.3031 (7)	8.5 (3)
O(10)	−0.1946 (8)	1.0576 (3)	0.1625 (6)	6.2 (3)
O(101)	−0.255 (1)	1.0501 (4)	−0.0105 (6)	8.6 (4)
C(1)	−0.268 (2)	0.7202 (6)	0.241 (1)	8.6 (6)
C(2)	−0.293 (2)	0.7123 (5)	0.360 (1)	8.1 (5)
C(3)	−0.296 (1)	0.7739 (5)	0.4129 (9)	6.5 (4)
C(4)	−0.163 (1)	0.8123 (4)	0.3868 (8)	5.1 (4)
C(5)	−0.128 (1)	0.8131 (4)	0.2652 (8)	4.9 (3)
C(6)	0.025 (1)	0.8358 (4)	0.2388 (7)	3.9 (3)
C(61)	0.212 (1)	0.7585 (6)	0.2372 (9)	7.0 (4)
C(62)	0.291 (1)	0.7151 (5)	0.310 (1)	8.1 (5)
C(7)	0.057 (1)	0.9007 (4)	0.2686 (8)	4.2 (3)
C(71)	0.308 (1)	0.9135 (5)	0.3355 (9)	5.9 (4)
C(72)	0.468 (1)	0.9106 (6)	0.301 (1)	8.0 (5)
C(8)	−0.028 (1)	0.9478 (4)	0.2029 (7)	4.7 (3)
C(81)	−0.158 (1)	0.9175 (5)	0.0437 (8)	5.6 (4)
C(82)	−0.139 (2)	0.9031 (6)	−0.0732 (8)	8.2 (5)
C(9)	0.038 (1)	1.0098 (4)	0.2049 (8)	5.7 (4)
C(91)	0.157 (1)	1.0582 (5)	0.3538 (9)	6.2 (4)
C(92)	0.135 (2)	1.0762 (7)	0.469 (1)	9.8 (6)
C(10)	−0.040 (1)	1.0566 (6)	0.137 (1)	6.7 (4)
C(101)	−0.294 (1)	1.0556 (5)	0.080 (1)	6.2 (4)
C(102)	−0.450 (1)	1.0601 (6)	0.119 (1)	7.5 (5)
C(11)	−0.401 (2)	0.7597 (8)	0.088 (1)	12.7 (8)

Table 2. *Selected bond lengths ($\mathring{A}$), valency angles (°) and torsion angles (°)*

O(1)—C(1)	1.42 (2)	C(1)—C(2)	1.51 (2)
O(3)—C(3)	1.22 (1)	C(2)—C(3)	1.51 (2)
O(5)—C(1)	1.42 (2)	C(3)—C(4)	1.50 (2)
O(5)—C(5)	1.43 (1)	C(4)—C(5)	1.55 (1)
O(6)—C(6)	1.43 (1)	C(5)—C(6)	1.49 (1)
O(7)—C(7)	1.45 (1)	C(6)—C(7)	1.51 (1)
O(8)—C(8)	1.45 (1)	C(7)—C(8)	1.53 (1)
O(9)—C(9)	1.45 (1)	C(8)—C(9)	1.49 (1)
O(10)—C(10)	1.42 (1)	C(9)—C(10)	1.51 (2)

C(1)—O(1)—C(11)	116 (1)	O(3)—C(3)—C(4)	123 (1)
C(1)—O(5)—C(5)	116.5 (9)	C(2)—C(3)—C(4)	114 (1)
O(1)—C(1)—O(5)	110 (1)	C(3)—C(4)—C(5)	112.3 (8)
O(1)—C(1)—C(2)	106 (1)	O(5)—C(5)—C(4)	110.6 (8)
O(5)—C(1)—C(2)	111 (1)	O(5)—C(5)—C(6)	105.3 (8)
C(1)—C(2)—C(3)	109 (1)	C(4)—C(5)—C(6)	113.9 (8)
O(3)—C(3)—C(2)	123 (1)		

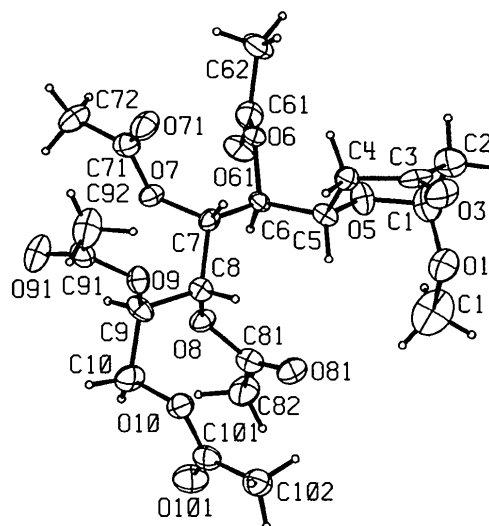|			
C(11)—O(1)—C(1)—O(5)	67 (1)	C(1)—C(2)—C(3)—O(3)	124 (1)
C(5)—O(5)—C(1)—O(1)	57 (1)	C(1)—C(2)—C(3)—C(4)	− 52 (1)
C(5)—O(5)—C(1)—C(2)	− 60 (1)	O(3)—C(3)—C(4)—C(5)	− 129 (1)
C(1)—O(5)—C(5)—C(4)	53 (1)	C(2)—C(3)—C(4)—C(5)	47 (1)
O(5)—C(1)—C(2)—C(3)	56 (1)	C(3)—C(4)—C(5)—O(5)	− 45 (1)

Fig. 1. *ORTEP*II (Johnson, 1971) drawing showing atom numbering. The non-H atoms are represented by 30% probability ellipsoids.

groups oriented *sc, sc, ap, − sc* to each other, respectively. The OAc group at the C(6) atom has the energetically preferred − *sc* conformation (Pérez, St-Pierre & Marchessault, 1978) with the O(5)—C(5)—C(6)—O(6) torsion angle at − 64.5 (9)°, while the C(7) atom is *ap* oriented to the O(5) acetal-ring O atom. The O(3) atom from the keto group is in the pseudo-equatorial position with the C(1)—C(2)—C(3)—O(3) torsion angle at − 129 (1)°. The orientation of the methoxy group at the anomeric centre is determined by the *exo*-anomeric effect (Jeffrey, 1979). All bond lengths and valency angles have normal values.

In the crystal under investigation no significant steric interactions were observed. Empirical force-field calculations using the *MM*2(85) program (Allinger, 1987) for this compound reproduced almost ideally the experimentally determined geometry of the molecule. The molecular-mechanics study revealed only one difference between calculated and observed results. The theoretically predicted orientation of the acyl residue at the O(10) atom is *ap* [the C(9)—C(10)—O(10)—C(101) torsion angle is − 174.1°] and that observed in the crystal is − *ac* [− 131.2 (9)°]. This first value seems to be less adequate knowing the tendency of the OAc groups in carbohydrate structures to lie coplanar with one vicinal H atom (*i.e.* ± *ac* conformation).

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Structure of an *anti*-Aldol Addition Product of Benzaldehyde and a Pseudoephedrine-Derived *O*-Silyl Ketene *N*,*O*-Acetal

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Abstract. [4*S*-(4*R**,5*R**,8*R**,9*S**)]-2,2,5,6,8-Penta-methyl-4,9-diphenyl-1,3-dioxa-6-aza-2-silacyclono-nan-7-one, $C_{22}H_{29}NO_3Si$, $M_r = 383.56$, monoclinic, $P2_1$, $a = 6.550$ (3), $b = 17.318$ (6), $c = 20.129$ (6) Å, $\beta = 98.83$ (3)°, $V = 2256.2$ (14) Å^3, $Z = 4$, $D_x = 1.13$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.18$ cm^{-1}, $F(000) = 824$, room temperature, R on $F = 0.039$ for 4305 reflections with $F_o^2 > 3\sigma(F_o^2)$. The two independent molecules in this structure have nearly the same configuration and geometry. The Si atoms are tetrahedrally coordinated, with average Si—C bond distances of 1.842 (3) Å and average Si—O bond distances of 1.636 (7) Å; angles at Si differ from 109.5° by an average of 3.5°. The nine-membered rings are fully extended and the planes of the phenyl groups are approximately perpendicular to the nine-membered ring.

Introduction. Further studies of the reactions of *O*-silyl ketene *N*,*O*-acetals with aldehydes have revealed interesting aspects of the mechanism of the transformation (Myers, Widdowson & Kukkola, 1992). Crucial to these studies is the fact that (*S*,*S*)-pseudoephedrine-derived *O*-silyl ketene *N*,*O*-acetal (1) reacts readily with benzaldehyde to form product (2), whereas the corresponding ephedrine-derived acetal does not react. The structure of *anti*-aldol product (2), described herein, is similar to that derived from *S*-prolinol, previously reported (Schaefer, Widdowson & Myers, 1991; Myers &

Widdowson, 1990) and provides further support for the proposed mechanism involving hypervalent organosilicon intermediates (Myers, Widdowson & Kukkola, 1992; Myers & Widdowson, 1990).

(1)   (2)
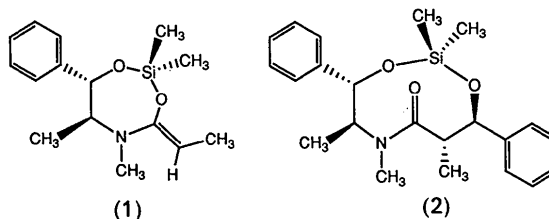
Experimental. A tablet-shaped crystal, 0.15 × 0.51 × 0.61 mm, was used for data collection on a CAD-4 diffractometer with ω scans. 25 reflections with $25 < 2\theta < 32°$ were used for determination of the cell dimensions. No absorption correction was made. $(\sin\theta/\lambda)_{max} = 0.54$ Å^{-1}; h from -7 to 7, k from -18 to 18, l from -19 to 19. Three standard reflections (05$\bar{5}$, 1$\bar{1}$4 and 01$\bar{8}$) showed no variations greater than those predicted by counting statistics. 6162 reflections were measured, of which 5887 were independent. Goodness of fit for merging was 0.87 ($R_{merge} = 0.019$ for 177 reflections with exactly two observations). All reflections were used in solution and refinement of the structure. The Si atoms were found from a Patterson map and the remaining atoms located by successive structure factor–Fourier calculation; the y coordinate of atom Si1 was fixed at 0.7 to define the origin. F_o^2 magnitudes were used in

† Contribution No. 8513.