

Structure of an Allylic Precursor of Higher Sugars

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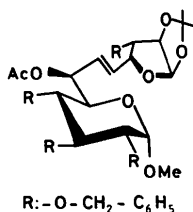
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Abstract. 3-*O*-Benzyl-5-deoxy-1,2-*O*-isopropylidene-5-*C*-[methyl (*E*)-6-*O*-acetyl-2,3,4-tri-*O*-benzyl-7-deoxy-*L*-glycero- α -D-gluco-heptopyranosid-7-ylidene]- α -D-xylo-furanose, C₄₆H₅₂O₁₁, *M*_r = 780.91, monoclinic, *P*2₁, *a* = 5.870 (1), *b* = 31.511 (6), *c* = 11.454 (2) Å, β = 91.63 (1)°, *V* = 2118 (1) Å³, *Z* = 2, *D*_x = 1.225 Mg m⁻³, λ (Cu *K* α) = 1.5418 Å, μ = 0.719 mm⁻¹, *F*(000) = 832, room temperature, *R* = 0.049 for 3785 reflections with *I* > 2 σ (*I*). The two saccharide moieties are linked *via* an allylic chain. The pyranoid ring is attached to the chiral [*S*(*L*)] carbon atom which is *trans* to the furanoid ring across the allylic double bond.

Introduction. Allylic alcohols substituted at both ends of the allylic system with two different monosaccharide subunits are convenient precursors for the preparation of higher sugars. Recently the general route to such allylic alcohols was developed (Jarosz, 1987*a,b*, 1988*a,b*). The first structure from this series, with the propynyl bridge between two pyranosides, was published by Krajewski *et al.* (1985). The crystal structure of the title compound (see Scheme 1) was undertaken to determine the relative conformation of both carbohydrate moieties and to verify the absolute configuration of the new chiral centre at C(6) which was assigned by chemical correlation.



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Experimental. The title compound was obtained and recrystallized by the method previously reported (Jarosz, 1988*a*).

Crystal dimensions 0.5 × 0.5 × 0.8 mm, DEC micro PDP 11-controlled Stoe-AED diffractometer, Ni-filtered Cu *K* α radiation. Lattice parameters from 45 reflections (30 ≤ 2 θ ≤ 40°). $\omega/2\theta$ scan, 5 ≤ 2 θ ≤ 127°, 0 ≤ *h* ≤ 6, 0 ≤ *k* ≤ 36, -13 ≤ *l* ≤ 13, two standard reflections: no variation. 3907 independent reflections measured [(sin θ / λ)_{max} = 0.5804 Å⁻¹], 3838 with *I* > 2 σ (*I*) considered observed. No absorption correction. Structure solved by direct methods and refined (on *F*'s) with isotropic and then with anisotropic temperature factors by the least-squares method. Some of the H-atom positions were calculated based on the geometry of the molecules (C—H and N—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 513 non-H-atom parameters converged with *R* = 0.049 and *wR* = 0.046, final (Δ/σ)_{max} ≤ 0.053, -0.25 ≤ $\Delta\rho$ ≤ 0.24 e Å⁻³, *w* = 1/ σ^2 (*F*). The final atomic parameters are given in Table 1.† All crystallographic computations were performed on a VAX/VMS V4.6 computer using programs *SHELXS86* (Sheldrick, 1986), *XTAL2.2* (Hall & Stewart, 1987) with the neutral atom scattering factors and anomalous-dispersion corrections as included in the program, the *XTAL*

† Lists of structure factors, anisotropic temperature factors, H-atom parameters, interatomic distances and valency angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52279 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional ($\times 10^4$) and thermal parameters ($\times 10^3$) with e.s.d.'s in parentheses
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
O(1)	3971 (5)	4331	7236 (2)	70 (1)
O(2)	6925 (5)	3703 (1)	7907 (3)	71 (1)
O(3)	5573 (5)	3566 (1)	10253 (2)	68 (1)
O(4)	1863 (6)	4144 (1)	10894 (2)	77 (1)
O(5)	5046 (5)	4755 (1)	8826 (2)	59 (1)
O(6)	4246 (5)	5146 (1)	10931 (2)	64 (1)
O(61)	1825 (8)	5487 (2)	12049 (3)	119 (2)
O(1')	-3378 (6)	5921 (1)	5436 (2)	87 (1)
O(2')	-2005 (6)	6496 (1)	6452 (2)	75 (1)
O(3')	-3774 (5)	6052 (1)	9200 (2)	65 (1)
O(4')	-2360 (5)	5554 (1)	7145 (2)	68 (1)
C(1)	5709 (7)	4440 (2)	8030 (3)	61 (1)
C(2)	6481 (7)	4043 (2)	8698 (4)	62 (1)
C(3)	4665 (7)	3893 (2)	9510 (3)	58 (1)
C(4)	3844 (7)	4260 (2)	10276 (3)	58 (1)
C(5)	3174 (6)	4631 (2)	9502 (3)	51 (1)
C(6)	2339 (6)	5025 (2)	10149 (3)	55 (1)
C(7)	1783 (7)	5367 (2)	9288 (3)	54 (1)
C(11)	3223 (10)	4678 (2)	6497 (4)	101 (2)
C(21)	9054 (9)	3699 (2)	7492 (6)	122 (3)
C(22)	9478 (8)	3346 (2)	6648 (4)	73 (2)
C(23)	11502 (8)	3339 (2)	6090 (4)	88 (2)
C(24)	11901 (9)	3032 (2)	5263 (5)	99 (2)
C(25)	10281 (11)	2731 (2)	5009 (5)	99 (2)
C(26)	8257 (10)	2735 (2)	5566 (5)	85 (2)
C(27)	7855 (8)	3043 (2)	6399 (4)	77 (2)
C(31)	4590 (12)	3163 (2)	10024 (5)	113 (3)
C(32)	5783 (9)	2844 (2)	10867 (4)	74 (2)
C(33)	7820 (10)	2674 (2)	10584 (5)	93 (2)
C(34)	8829 (10)	2372 (2)	11286 (7)	110 (3)
C(35)	7802 (13)	2236 (2)	12267 (6)	104 (3)
C(36)	5695 (12)	2405 (2)	12560 (4)	97 (2)
C(37)	4734 (9)	2714 (2)	11845 (5)	83 (2)
C(41)	2355 (15)	4006 (4)	12044 (6)	222 (5)
C(42)	354 (11)	4049 (3)	12785 (5)	95 (2)
C(43)	-963 (17)	3703 (3)	13000 (7)	129 (4)
C(44)	-2690 (17)	3717 (5)	13750 (10)	189 (6)
C(45)	-2907 (26)	4089 (6)	14350 (9)	189 (7)
C(46)	-1864 (26)	4444 (4)	14160 (10)	183 (6)
C(47)	4 (16)	4407 (3)	13360 (8)	143 (4)
C(61)	3737 (10)	5376 (2)	11867 (4)	76 (2)
C(62)	5816 (11)	5472 (2)	12575 (5)	112 (3)
C(1')	-3832 (7)	5850 (2)	6589 (4)	62 (1)
C(2')	-3468 (7)	6274 (2)	7197 (3)	60 (1)
C(3')	-2207 (7)	6164 (1)	8332 (3)	53 (1)
C(4')	-897 (7)	5768 (2)	7988 (3)	55 (1)
C(5')	-315 (7)	5461 (2)	8953 (3)	55 (1)
C(6')	-2158 (8)	6312 (2)	5307 (4)	71 (2)
C(7')	-3553 (9)	6591 (2)	4494 (4)	87 (2)
C(8')	196 (11)	6237 (3)	4902 (5)	128 (3)
C(31')	-4576 (9)	6404 (2)	9850 (4)	88 (2)
C(32')	-2868 (9)	6605 (2)	10676 (4)	69 (2)
C(33')	-962 (9)	6386 (2)	11066 (4)	76 (2)
C(34')	613 (10)	6582 (2)	11808 (4)	92 (2)
C(35')	329 (14)	6983 (2)	12167 (5)	107 (3)
C(36')	-1601 (15)	7211 (2)	11804 (5)	108 (3)
C(37')	-3169 (12)	7020 (2)	11050 (4)	98 (2)

version of ORTEPII (Johnson, 1971), and PUCK2 (Luger & Bülow, 1983).

Discussion. The numbering scheme and overall conformation are shown in Fig. 1, selected bond lengths, valency angles and torsion angles are presented in Table 2.

The Cremer & Pople (1975) ring-puckering parameters indicate the 4C_1 chair conformation for the pyranoid ring [$Q = 0.569$ (4) \AA , $\theta = 4.6$ (4) and $\varphi = 243.7$ (8) $^\circ$] and a hybrid ${}^3T_4 + {}^3E$, ${}^1T_2 + {}_2E$ conformation for the fused-ring system of 1,2-*O*-isopropylidene- α -D-xylo-furanose [$q_2 = 0.329$ (5) \AA , $\varphi = 296.3$ (8) $^\circ$ for the furanoid ring and $q_2 =$

0.212 (5) \AA , $\varphi = 245$ (1) $^\circ$ for the 1,2-*O*-isopropylidene ring]. In this nomenclature symbols before the comma refer to the furanoid ring (Krajewski, Gluziński, Urbańczyk-Lipkowska, Banaszek & Dobler, 1984). The conformation of these five-membered fused rings differs from other similar systems (Klaska, Jarchow, Günther & Paulsen, 1978; Kashino, Inokawa, Haisa, Yasuoka & Kakudo, 1981; Taga, Kaji & Osaki, 1982; Krajewski *et al.*, 1984, and references therein) in which the furanoid moieties have a 'pure' twist or envelope conformation. But, as was pointed out earlier, the interconformational energy barriers in these systems are low and the conformations may be affected seriously by substituents (Krajewski *et al.*, 1984).

The bond lengths and valency angles of the allylic chain and of both carbohydrate units are normal. The geometry of the acetal sequence C(5)—O(5)—C(1)—O(1)—C(11) shows the characteristic bond length and valency angle variations observed in methyl pyranosides and was predicted from theoretical calculations (Jeffrey, Pople, Binkley & Vishveshwara, 1978). The *O*-benzyl side groups have large values for the temperature factors but only the valency angles of the group at C(4) differ more than 3σ from the value 120° .

The absolute configuration of the chiral centre at C(6) was determined as *S*(*L*-glycero) with reference to the carbohydrate moieties.

The acetoxy group at C(6) has normal orientation, similar to acetylated hexopyranosides (Pérez, St-Pierre & Marchessault, 1978), and the allylic chain has the synclinal/anticlinal orientation with regard to the C(5)—O(5) bond in the pyranoid ring and the exocyclic C(5)—C(6) bond, respectively [the torsion

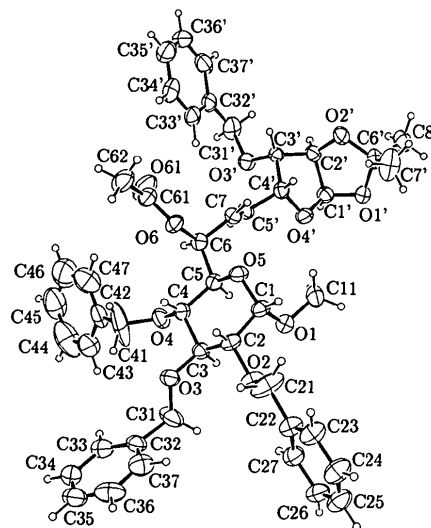


Fig. 1. ORTEP drawing of the molecular structure with crystallographic numbering scheme. The ellipsoids correspond to 30% probability contours of atomic displacement.

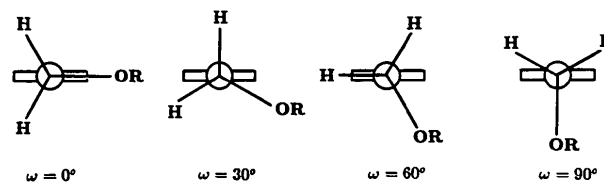
Table 2. Selected interatomic distances (Å), valency angles (°) and dihedral angles (°), with *e.s.d.*'s in parentheses

O(1)—C(1)	1.390 (5)	O(3')—C(31')	1.422 (7)
O(1)—C(11)	1.444 (6)	O(4')—C(1')	1.410 (6)
O(2)—C(2)	1.431 (6)	O(4')—C(4')	1.442 (5)
O(2)—C(21)	1.350 (6)	C(1)—C(2)	1.527 (7)
O(3)—C(3)	1.429 (6)	C(2)—C(3)	1.511 (6)
O(3)—C(31)	1.415 (7)	C(3)—C(4)	1.538 (6)
O(4)—C(4)	1.426 (5)	C(4)—C(5)	1.512 (6)
O(4)—C(41)	1.409 (8)	C(5)—C(6)	1.534 (6)
O(5)—C(1)	1.411 (6)	C(6)—C(7)	1.491 (6)
O(5)—C(5)	1.418 (5)	C(7)—C(5')	1.313 (6)
O(6)—C(6)	1.465 (5)	C(61)—C(62)	1.478 (8)
O(6)—C(61)	1.333 (6)	C(1')—C(2')	1.520 (7)
O(61)—C(61)	1.200 (8)	C(2')—C(3')	1.518 (6)
O(1')—C(1')	1.374 (5)	C(3')—C(4')	1.525 (6)
O(1')—C(6')	1.437 (7)	C(4')—C(5')	1.501 (6)
O(2')—C(2')	1.413 (5)	C(6')—C(7')	1.505 (7)
O(2')—C(6')	1.434 (5)	C(6')—C(8')	1.490 (8)
O(3')—C(3')	1.418 (5)		
C(1)—O(1)—C(11)	113.7 (3)	O(6)—C(6)—C(7)	111.4 (4)
C(2)—O(2)—C(21)	114.6 (4)	C(5)—C(6)—C(7)	109.5 (3)
C(3)—O(3)—C(31)	113.1 (4)	C(6)—C(7)—C(5')	122.8 (4)
C(4)—O(4)—C(41)	113.2 (5)	O(6)—C(61)—O(61)	122.0 (5)
C(1)—O(5)—C(5)	112.9 (4)	O(6)—C(61)—C(62)	110.6 (5)
C(6)—O(6)—C(61)	116.7 (4)	O(61)—C(61)—C(62)	127.4 (5)
C(1')—O(1')—C(6')	110.4 (3)	O(4')—C(1')—O(1')	114.1 (4)
C(2')—O(2')—C(6')	109.2 (4)	O(4')—C(1')—C(2')	107.4 (3)
C(3')—O(3')—C(31')	113.8 (4)	O(1')—C(1')—C(2')	105.6 (4)
C(1')—O(4')—C(4')	109.8 (4)	O(2')—C(2')—C(3')	109.9 (3)
O(1)—C(1)—O(5)	112.7 (3)	O(2')—C(2')—C(1')	103.8 (3)
O(1)—C(1)—C(2)	109.2 (4)	O(1')—C(2')—C(3')	104.5 (4)
O(5)—C(1)—C(2)	109.7 (3)	O(3')—C(3')—C(2')	110.3 (3)
O(2)—C(2)—C(1)	110.6 (3)	C(2')—C(3')—C(4')	101.7 (3)
O(2)—C(2)—C(3)	107.4 (4)	O(3')—C(3')—C(4')	108.6 (4)
C(1)—C(2)—C(3)	111.2 (4)	O(4')—C(4')—C(3')	105.2 (3)
O(3)—C(3)—C(2)	109.6 (3)	O(4')—C(4')—C(5')	108.1 (4)
O(3)—C(3)—C(4)	108.7 (3)	C(3')—C(4')—C(5')	116.3 (3)
C(2)—C(3)—C(4)	110.6 (4)	C(7)—C(5')—C(4')	123.5 (4)
O(4)—C(4)—C(3)	111.3 (4)	O(2')—C(6')—O(1')	105.8 (3)
O(4)—C(4)—C(5)	106.6 (3)	O(2')—C(6')—C(7')	110.4 (4)
C(3)—C(4)—C(5)	109.1 (3)	O(2')—C(6')—C(8')	108.3 (4)
O(5)—C(5)—C(4)	110.0 (3)	O(1')—C(6')—C(7')	107.5 (4)
O(5)—C(5)—C(6)	107.6 (4)	O(1')—C(6')—C(8')	111.3 (5)
C(4)—C(5)—C(6)	115.1 (3)	C(7')—C(6')—C(8')	113.2 (4)
O(6)—C(6)—C(5)	104.9 (3)		
C(1)—O(5)—C(5)—C(6)	-169.3 (3)	C(1)—C(2)—C(3)—C(4)	-50.9 (4)
O(5)—C(5)—C(6)—O(6)	-63.8 (4)	C(2)—C(3)—C(4)—C(5)	52.1 (4)
O(5)—C(5)—C(6)—C(7)	55.8 (4)	C(3)—C(4)—C(5)—O(5)	-57.6 (4)
C(5)—C(6)—O(6)—C(61)	-156.7 (4)	C(4)—C(5)—O(5)—C(1)	64.6 (4)
C(5)—C(6)—C(7)—C(5')	102.5 (5)	C(5)—O(5)—C(1)—C(2)	-62.0 (4)
C(6)—C(7)—C(5')—C(4')	-172.6 (4)	O(4')—C(1')—C(2')—C(3')	-15.7 (4)
C(7)—C(5')—C(4')—O(4')	125.0 (4)	C(1')—C(2')—C(3')—C(4')	29.5 (4)
C(5')—C(4')—O(4')—C(1')	150.3 (3)	C(2')—C(3')—C(4')—O(4')	-33.6 (4)
C(5)—O(5)—C(1)—O(1)	59.9 (4)	C(3')—C(4')—O(4')—C(1')	25.4 (4)
O(5)—C(1)—O(1)—C(11)	62.1 (5)	C(4')—O(4')—C(1')—C(2')	-6.1 (4)
O(5)—C(1)—C(2)—C(3)	54.5 (4)		

angles O(5)—C(5)—C(6)—C(7) and C(5)—C(6)—C(7)—C(5') are 55.8 (4) and 102.5 (5)°, respectively]. The double bond in the allylic chain is *trans* and has the anticlinical orientation with regard to the C(4')—O(4') bond in the furanoid ring [the torsion angle C(7)—C(5')—C(4')—O(4') is 125.0 (4)°].

The *O*-benzyl groups in the title compound correspond to three out of four possible conformations of benzyl alcohol and its ethers (Ito & Hirota, 1981; see Scheme 2). The group at C(2) [with dihedral angle O(2)—C(21)—C(22)—C(27) = -4.0 (8)°] corresponds to a variant with a coplanar oxygen atom and aromatic ring ($\omega = 0^\circ$), the groups at C(3) and C(4) [respective dihedral angles O(3)—C(31)—C(32)—C(33) and O(4)—C(41)—C(42)—C(47) are

-82.9 (6) and -89.1 (9)°] to a variant with the oxygen atom perpendicular to an aromatic ring ($\omega = 90^\circ$), and the group at C(3') [with O(3')—C(31')—C(32')—C(33') = -20.8 (7)°] is close to a variant with one hydrogen atom from the methylene group perpendicular to an aromatic ring ($\omega = 30^\circ$). There is no conformation with coplanar hydrogen atom and aromatic ring ($\omega = 60^\circ$). The C(*i*)—O(*i*)—C(*i*1)—C(*i*2) torsion angles (*i* = 2,3,4) are close to 180° [-179.0 (4), 178.5 (4) and 157.8 (6)°, respectively] but in the case of the furanoside residue (*i* = 3') this angle is -70.6 (5)°.



Inspection of conformations of the *O*-benzyl moieties as side groups in other crystal structures of carbohydrates (Boeyens, Brink, Hall, Jordaan & Pretorius, 1977; Cesario, Guilhem & Martin, 1979; Luger & Paulsen, 1981; Kashino *et al.*, 1981; Krajewski, Gryniewicz, Gluźniński, Urbańczyk-Lipkowska, Zamojski & Stadnicka, 1982; Krajewski, Urbańczyk-Lipkowska, Gluźniński, Zamojski & Stadnicka, 1983; Krajewski *et al.*, 1985; Carroll, Mandel & Mandel, 1983; Strumpel, Schmidt, Luger & Paulsen, 1984; Vorontsova, Dekaprilevich & Chizhov, 1985; Kiss, Wyss, Flesch, Arnold, Noack & Schonholzer, 1985; Billington, Baker, Kulagowski & Mawer, 1987) shows that one O—C—C—C torsion angle is close to 0, 30, 60 or 90°, and the C—O—C—C torsion angles in pyranosides have the average value 169° (22 cases) or 69° [2 cases, at C(1) and C(6)], and in furanosides 179° (1 case) or 67° (4 cases).

The *O*-benzyl groups connected with the pyranoid rings have all four conformations ($\omega = 0^\circ$, six groups; $\omega = 30^\circ$, six groups; $\omega = 60^\circ$, three groups; $\omega = 90^\circ$, nine groups) while the *O*-benzyl moieties connected with the furanoid rings have only two of them [$\omega = 30^\circ$, one group (the title compound); $\omega = 60^\circ$, four groups]. The results of the above inspection show that the *O*-benzyl moieties connected with pyranoid or furanoid rings have conformations similar to those of benzyl alcohol or its esters. Intermolecular interactions and/or interactions between different vicinal groups affect these conformations. The greatest deformations occur when a single *O*-benzyl moiety is connected with a ring. This is the case for all inspected furanosides.

In the investigated crystal there is one intramolecular steric interaction C(2')—H(2')...H(311')—

C(31') with a distance between the hydrogen atoms of 2.3 Å and several intermolecular contacts (≤ 2.6 Å) corresponding to van der Waals forces. Four atoms from the *O*-benzyl group connected with C(3') participate in these contacts.

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Structure of 3,6,10,12-Tetramethylbenzofuro[2,3-*b*]benzofuran

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Abstract. $C_{18}H_{18}O_2$, $M_r = 266.3$, monoclinic, $P2_1/n$, $a = 9.459$ (2), $b = 13.220$ (2), $c = 11.712$ (2) Å, $\beta = 98.92$ (2)°, $V = 1446.8$ (5) Å³, $D_m = 1.24$ (1), $D_x = 1.22$ g cm⁻³, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.73$ cm⁻¹, $T = 293$ K, $F(000) = 568$, $R = 0.077$ and $wR = 0.077$ for 1250 reflections with $F \geq 3\sigma(F)$. The furan rings are in envelope conformation with an angle of 66.5 (3)° between them.

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Introduction. The benzofuran ring system is prevalent in many natural products and some exhibit bactericidal activity (Gilchrist, 1985). The title compound was obtained as a by-product in the synthesis of pterocarpans (Ramakanth, 1984). The present paper reports the X-ray structure of the compound in the crystal.

Experimental. Colourless needle-shaped single crystals by slow evaporation of acetone, D_m by flotation, $0.35 \times 0.30 \times 0.25$ mm, monoclinic $P2_1/n$, three-