

Vratislav Langer,^{a*} Bohumil Steiner,^b Júlia Mičová^b and Miroslav Kož^b^aDepartment of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden, and^bInstitute of Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 38 Bratislava, SlovakiaCorrespondence e-mail:
langer@chem.chalmers.se

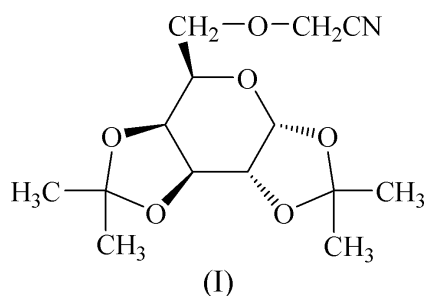
Key indicators

Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.038
 wR factor = 0.092
Data-to-parameter ratio = 14.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.6-*O*-Cyanomethyl-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose

The analysis of the title compound, $\text{C}_{14}\text{H}_{21}\text{NO}_6$, revealed a highly distorted conformation of the six-membered pyranose ring. The presence of two five-membered 1,3-dioxolane rings fused to the pyranose ring at the 1,2- and 3,4-positions is responsible for the severe deviation from the usual chair conformation of the pyranose ring. The three-dimensional packing is stabilized by weak hydrogen bonds of the $\text{C}-\text{H}\cdots\text{O}$ type.

Comment

Owing to a suitable protection of all secondary hydroxy groups, thus enabling selective modification at atoms C6 or O6 (replacement of OH or H), 1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose is an attractive intermediate for carbohydrate synthetic chemists. On the other hand, *O*-isopropylidene-galactose derivatives are valuable compounds in the study of the conformational behaviour of pyranose or furanose rings and their hydrogen-bonding patterns in the solid state. In this respect, many such structural analogues have been prepared and studied (Boeyens *et al.*, 1979; Engelhardt *et al.*, 1990; Krajewski *et al.*, 1990; Barnes & Brimacombe, 1991; Köll *et al.*, 1994; Čudić *et al.*, 1996; Cox *et al.*, 1996; Lakin *et al.*, 1996; Ojala *et al.*, 1996; Horton *et al.*, 1997; Imberty *et al.*, 1998).



We present here the single-crystal X-ray structure of the title compound, (I), containing a cyanomethyl group at atom O6. This derivative is an important intermediate for the preparation of the corresponding primary amine, carboxylic acid, amide or ester analogues. Because both substitution of hydroxy groups and stereochemical and conformational features of saccharide derivatives are closely connected to their biological properties, it is very important to know all the possible structural factors concerning these compounds.

The molecular structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. The presence of two 1,3-dioxolane rings fused to a pyranose ring imposes considerable conformational rigidity. The puckering parameters (Cremer & Pople, 1975) of $Q = 0.6399$ (15) Å, $\theta =$

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79.74 (13)° and $\varphi = 329.61$ (14)°, as well as the values of the relevant torsion angles [$O5-C1-C2-C3 = -12.98$ (19)°, $C1-C2-C3-C4 = 40.15$ (19)°, $C2-C3-C4-C5 = -13.67$ (19)°, $C3-C4-C5-O5 = -39.05$ (16)°, $C4-C5-O5-C1 = 70.74$ (14)° and $C5-O5-C1-C2 = -42.41$ (16)°], indicate that the O5/C1–C5 pyranose ring adopts a highly distorted conformation, which can be described as intermediate between a twist-boat, ${}^O T_2$, and screw-boat, ${}^O S_5$. Such severe deviations from the usual chair conformations of pyranose rings are rare but, regarding the mean values of the puckering parameters [$Q = 0.626$ Å, $\theta = 79.2^\circ$ and $\varphi = 324.4^\circ$] described previously (Köll *et al.*, 1994), seem to be common (with slight deviations) for di-*O*-isopropylidene-galactopyranose derivatives.

For the O1/C1/C2/O2/C9 five-membered 1,3-dioxolane ring, fused to the pyranose ring at the 1,2-position, the puckering parameters [$Q = 0.3123$ (15) Å and $\theta = 294.2$ (3)°] and the relevant torsion angles [$O1-C1-C2-O2 = -16.32$ (15)°, $C1-C2-O2-C9 = 31.25$ (14)°, $C2-O2-C9-O1 = -34.59$ (15)°, $O2-C9-O1-C1 = 23.91$ (16)° and $C9-O1-C1-C2 = -4.60$ (16)°] are indicative of a ${}^3 E$ (${}^{O2} E$) conformation, slightly distorted towards ${}^O T_4$ (${}^{O2} T_{C9}$). The second five-membered 1,3-dioxolane ring, (O3/C3/C4/O4/C12), fused to the pyranose ring at the 3,4-position, adopts a more distorted conformation. Considering the values of the relevant torsion angles [$O3-C3-C4-O4 = -14.94$ (15)°, $C3-C4-O4-C12 = -6.03$ (15)°, $C4-O4-C12-O3 = 24.82$ (15)°, $O4-C12-O3-C3 = -34.71$ (14)° and $C12-O3-C3-C4 = 30.54$ (14)°] and the puckering parameters [$Q = 0.3104$ (14) Å and $\theta = 171.4$ (3)°], this conformation can be described as intermediate between E_O (E_{O3}) and ${}^4 T_O$ (${}^{C12} T_{O3}$).

The mean value of the Csp^3-Csp^3 bond lengths within the pyranose moiety [1.530 (14) Å; see Table 1] is slightly longer than the values given for other saccharides (Jeffrey, 1990; Allen *et al.*, 1987), because the C1–C2, and especially C3–C4, bonds are longer than usual. Regarding the Csp^3-O distances, it is evident that the endocyclic C9–O1, C9–O2, C12–O3 and C12–O4 bonds of the 1,3-dioxolane rings are also longer [mean value 1.431 (1) Å; see Table 1] than in analogous bonds within the pyranose ring [mean value 1.418 (15) Å]. In contrast with previous observations for many α -pyranoses, where the anomeric C1–O1 bond is slightly shorter than the endocyclic C1–O5 bond (Jeffrey, 1990; Jeffrey & Taylor, 1980; Allen & Fortier, 1993), in (I) this tendency is reversed and the C1–O1 bond was found to be slightly longer than the C1–O5 bond (Table 1).

In the crystal structure of (I), two weak intermolecular C–H...O hydrogen bonds occur, with atoms C10 and C13 as donors, and atoms O4 and O6 as acceptors. This situation is illustrated in Fig. 2 and details of the hydrogen bonding are given in Table 2.

Experimental

Compound (I) was synthesized as the major product in the dehydration of the corresponding oxime (1,2:3,4-di-*O*-isopropylidene-6-*O*-hydroximinomethyl- α -D-galactopyranose, prepared in six steps

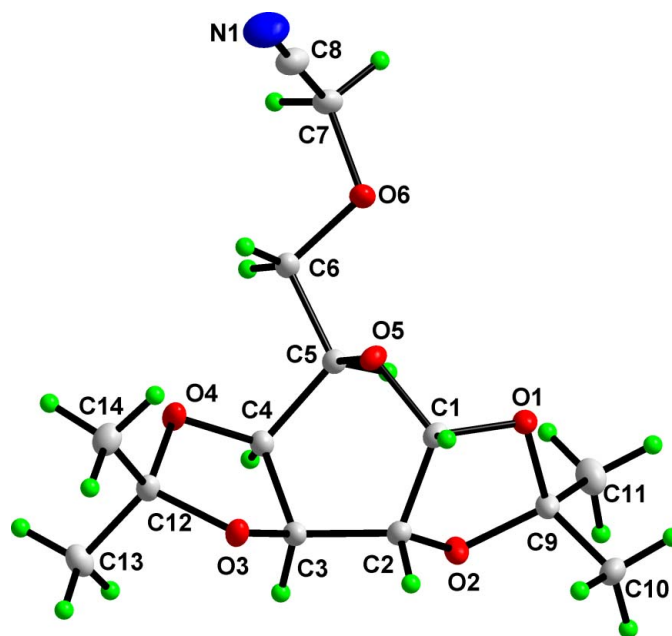


Figure 1
A perspective drawing of (I), showing the atom-numbering scheme. Atomic displacement ellipsoids are shown at the 30% probability level.

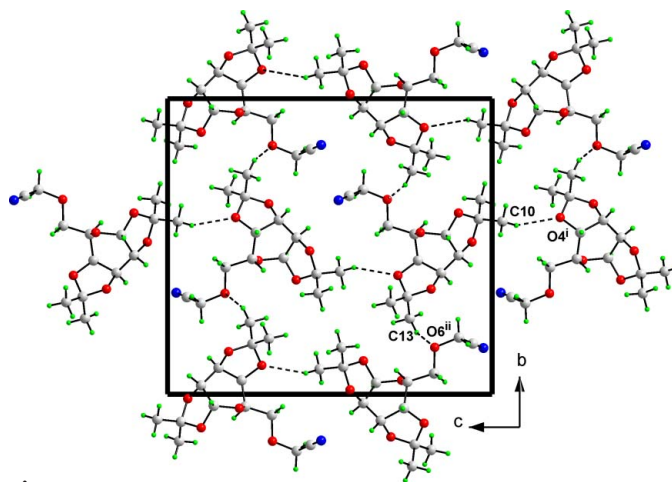


Figure 2
A projection of the structure of (I) along the *a* axis. Dashed lines indicate hydrogen bonds.

starting from D-galactose) using acetic anhydride as dehydrating agent (Koř & Steiner, 1996). Colourless single crystals of adequate quality for diffraction analysis were obtained by slow crystallization from a mixture of ethyl acetate/hexane, with cooling in a refrigerator.

Crystal data

$C_{14}H_{21}NO_6$
 $M_r = 299.32$
Orthorhombic, $P2_12_12_1$
 $a = 5.4596$ (1) Å
 $b = 15.9758$ (3) Å
 $c = 17.5111$ (3) Å
 $V = 1527.34$ (5) Å³
 $Z = 4$
 $D_x = 1.302$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 5866 reflections
 $\theta = 1.7-33.0^\circ$
 $\mu = 0.10$ mm⁻¹
 $T = 173$ (2) K
Needle, colourless
 $0.92 \times 0.12 \times 0.09$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	3210 independent reflections
ω scans	2609 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$R_{\text{int}} = 0.058$
$T_{\text{min}} = 0.912$, $T_{\text{max}} = 0.991$	$\theta_{\text{max}} = 33.0^\circ$
26 365 measured reflections	$h = -8 \rightarrow 8$
	$k = -24 \rightarrow 24$
	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.1721P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.092$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$
3210 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e } \text{\AA}^{-3}$
215 parameters	
Only H-atom displacement parameters refined	

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C1	1.4152 (17)	O5—C5	1.4281 (19)
O1—C9	1.4321 (18)	O6—C7	1.4097 (17)
O2—C9	1.4293 (18)	O6—C6	1.4285 (16)
O2—C2	1.4258 (19)	N1—C8	1.139 (3)
O3—C3	1.4266 (19)	C1—C2	1.538 (2)
O3—C12	1.4307 (17)	C2—C3	1.513 (2)
O4—C12	1.4321 (17)	C3—C4	1.545 (2)
O4—C4	1.4245 (17)	C4—C5	1.5241 (19)
O5—C1	1.4070 (16)	C5—C6	1.5152 (19)
C1—O1—C9	109.36 (11)	O5—C1—C2	114.16 (12)
C12—O4—C4	109.49 (10)	O2—C2—C1	103.85 (11)
C1—O5—C5	112.75 (11)	O4—C4—C3	104.14 (11)
O1—C1—C2	104.43 (11)	O5—C5—C4	110.22 (12)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10C \cdots O4 ⁱ	0.98	2.55	3.438 (2)	150
C13—H13B \cdots O6 ⁱⁱ	0.98	2.58	3.428 (2)	144

Symmetry codes: (i) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (ii) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$.

The crystals were very brittle and disintegrated into small needles when attempts were made to cut them; therefore, the crystal used was quite large in one dimension (0.92 mm). The absolute configuration at chiral atoms C1, C2, C3, C4 and C5 in (I) was taken as the known arrangement in the starting material, 1,2:3,4-di-O-isopropylidene- α -D-galactopyranose; because these atoms are not involved in the reaction steps during the preparation of (I), their configuration

remains unchanged. In the final cycles of refinement, in the absence of significant anomalous scattering effects, 2322 Friedel pairs were merged and $\Delta f''$ was set to zero. H atoms were constrained to an ideal geometry using an appropriate riding model. For secondary H atoms, the C—H distance was kept fixed at 0.99 \AA , and for tertiary H atoms, 1.00 \AA . For the methyl groups, the C—H distances (0.98 \AA) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting position based on the threefold averaged circular Fourier synthesis.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2004); software used to prepare material for publication: SHELXTL.

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