Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1230). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 6-*O*-[(*R*)-1-Carboxyethyl]-α-D-galactopyranoside

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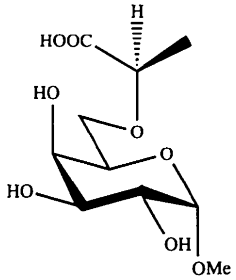
Abstract

The structure of the *O*-methyl glycoside of the naturally occurring 6-*O*-[(*R*)-1-carboxyethyl]-α-D-galactopyranose, $C_{10}H_{18}O_8$, has been determined. The absolute configuration was considered as *R* at the 1-carboxyethyl moiety which had previously been assigned by synthesis. This absolute configuration is consistent both with the determined Flack parameter [0.04 (43)] and the previously known configuration of D-galactose. The conformation of the torsion angle ω, O5—C5—C6—O6, is shown to be *gauche–trans*.

Comment

Substituents on sugar residues play an important biological role as modifiers of the parent carbohydrate compound (van Boeckel & Petitou, 1993). These substituents range from acetates, phosphates and sulfates to amino acids, pyruvates and lactates. Lactic acid substituents have been found to have both the (*R*) and (*S*) configuration in nature and can substitute sugar residues at different positions.

The capsular polysaccharide from *Butyrivibrio fibrisolvens* strain X6C61 contains a D-galactose residue with a 1-carboxyethyl group in the 6-position (Andersson, Ratnayake, Kenne, Ericsson & Stack, 1993). The synthesis of 1-carboxyethyl-substituted monosaccharides and their NMR and CD spectroscopy characterizations have recently been described (Andersson, Kenne, Stenutz & Widmalm, 1994), including those of the title compound, (I).



(I)

In oligosaccharides the major degrees of freedom are observed at the glycosidic linkage. The available conformational space can be monitored by the torsion angles φ, here defined by H1—C1—O1—C10, and ψ which are also most conveniently used for describing a certain conformer. In the case of 6-substitution an additional torsion angle ω, defined by O5—C5—C6—O6, is of paramount importance for the overall three-dimensional structure.

The title compound (I) is substituted at position 6 by a 1-carboxyethyl group, and three dihedral angles are of major interest. The ω torsion angle [76.4 (5)°] is *gauche–trans* which has been shown to be the preferred conformation in crystal structures having the *galacto* configuration, as in the present molecule.

In the case of the *gluco* configuration, the *gauche–gauche* conformer is the most abundant in the crystal state (Marchessault & Perez, 1979). The torsion angle φ, defined above, has a value of −45.4 (3)°, *i.e.* the staggered conformer where the exoanomeric effect contributes to energy stabilization.

The torsion angle φ′, defined by H8—C8—O6—C6 [−34.7 (3)°], has a *gauche*(−) conformation and the torsion angle ψ′ defined by C8—O6—C6—C5 [170.8 (4)°] has an *anti* conformation. The latter conformation gives an overall extended three-dimensional shape of (I) with

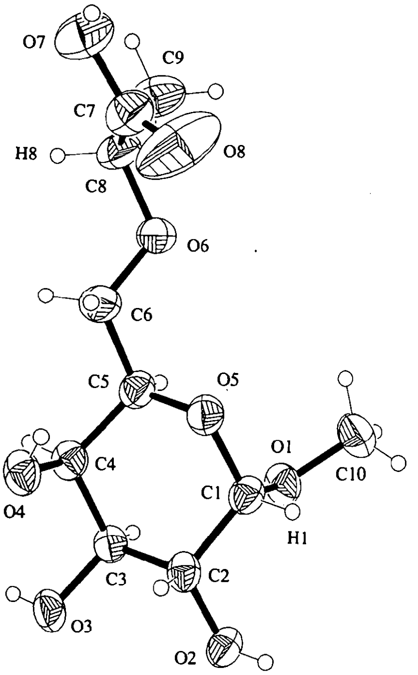


Fig 1. Perspective view and atomic numbering of (I) with 50% probability ellipsoids. H atoms are drawn as small circles of arbitrary radius.

the 1-carboxyethyl substituent group pointing outwards from the galactose residue.

The observed configuration of the 1-carboxyethyl group, (*R*), is consistent with inversion of configuration at the secondary position of (*S*)-2-chloropropionic acid on etherification by O6 of the galactose residue.

The e.s.d. of the Flack parameter (Flack, 1983) seems too high to verify that the correct absolute configuration has been chosen. However, the value of 0.04 is close to zero and thus indicates the correct absolute configuration. If the Flack parameter were to indicate a mirror image, the value would be 2.2 e.s.d.'s away from unity. We claim that it is more likely that we have chosen the correct configuration rather than the mirror image, both with respect to the value of the Flack parameter and with the premise that the synthesis of the title compound was from methyl α-D-galactopyranoside with known absolute configuration. The observation that this configuration is retained in (I) thus concludes that the absolute configuration is correct.

The crystal structure of (I) is stabilized by several intermolecular hydrogen bonds. There are four short intermolecular O···O distances [O2···O3($2-x$, $y-\frac{1}{2}$, $2-z$) 2.81 (1), O2···O4($1-x$, $y-\frac{1}{2}$, $2-z$) 2.80 (1), O3···O4($2-x$, $y-\frac{1}{2}$, $2-z$) 2.83 (1) and O6···O7($1-x$, $y-\frac{1}{2}$, $3-z$) 2.93 (1) Å] indicating possible hydrogen bonds. The one of special interest for the present investigation is O6···O7 where the position of H7 is geometrically restricted. The angle O6···H7—O7($1-x$, $y-\frac{1}{2}$, $3-z$), 177.0 (1)°, is consistent with hydrogen-bond formation and O6 acts as the acceptor. Another close intermolecular O···O contact, O7···O8($1-x$, $y+\frac{1}{2}$, $3-z$) [2.96 (1) Å], does not participate in any hydrogen bonding since the angle O7—H7···O8($1-x$, $y+\frac{1}{2}$, $3-z$) [111 (1)°] is too small. In the present study, one cannot deduce any donor–acceptor scheme for the first three intermolecular O···O contacts above. Finally there are two longer intermolecular O···O contacts [O1···O3($2-x$, $y-\frac{1}{2}$, $2-z$), 3.23 and O2···O5($1-x$, $y-\frac{1}{2}$, $2-z$), 3.32 Å] but as a result of the longer distance, these two O-atom pairs contribute little to the hydrogen bonding. The O7—H7···O6 hydrogen bond is shown in Fig. 2. There is a chain of similar hydrogen bonds towards neighbouring molecules.

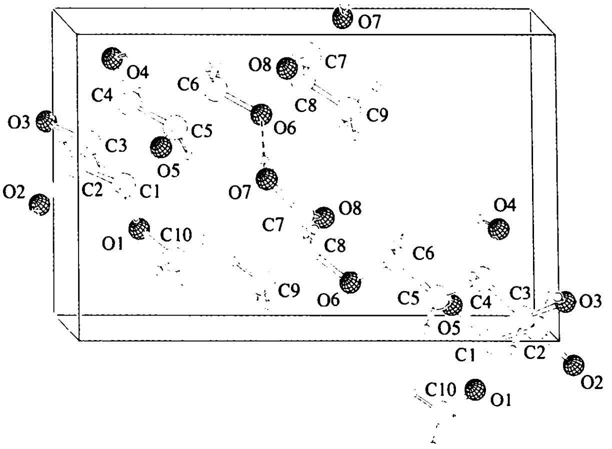


Fig 2. Perspective view (*SCHAKAL*; Keller, 1992) of two molecules of (I) showing the close contact O7—H7···O6 responsible for one of the hydrogen bonds. H atoms are drawn as small circles of arbitrary radius.

Experimental

The synthesis of compound (I) has been described previously (Andersson, Kenne, Stenutz & Widmalm, 1994). Crystallization of (I), as its protonated form, was from a thick aqueous syrup; crystals formed upon standing at ambient temperature.

Crystal data

$C_{10}H_{18}O_8$
$M_r = 266.24$
Monoclinic
$P2_1$
$a = 5.840\ (3)$ Å
$b = 8.063\ (6)$ Å
$c = 12.923\ (7)$ Å
$\beta = 101.74\ (6)°$
$V = 595.8\ (6)$ Å^3
$Z = 2$
$D_x = 1.484$ Mg m^{-3}

Cu *Kα* radiation
$\lambda = 1.54184$ Å
Cell parameters from 24 reflections
$\theta = 17.70$–$26.44°$
$\mu = 1.122$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.25 × 0.20 × 0.15 mm
Colourless

Data collection

Stoe AED-4 diffractometer
$\omega/2\theta$ scans

1516 observed reflections
[$I > 2\sigma(I)$]

Absorption correction: ψ scans (North, Phillips & Matthews, 1968)
$T_{\min} = 0.567$, $T_{\max} = 0.750$
4008 measured reflections
2045 independent reflections

$R_{\rm int} = 0.0673$
$\theta_{\max} = 68.36°$
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 8$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 90 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0562$
$wR(F^2) = 0.1411$
$S = 1.111$
2045 reflections
164 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0940P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.236$ e Å^{-3}
$\Delta\rho_{\min} = -0.307$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0269 (40)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.04 (43)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
C1	0.5618 (7)	0.9615 (5)	1.1232 (3)	0.0350 (9)
O1	0.6659 (5)	0.8106 (4)	1.1609 (2)	0.0402 (7)
C10	0.5357 (11)	0.7218 (7)	1.2247 (4)	0.0589 (14)
C2	0.6719 (7)	1.0163 (5)	1.0314 (3)	0.0329 (9)
O2	0.6529 (5)	0.8903 (4)	0.9530 (2)	0.0377 (7)
C3	0.9236 (6)	1.0696 (5)	1.0707 (3)	0.0318 (9)
O3	1.0239 (5)	1.1320 (4)	0.9872 (2)	0.0412 (8)
C4	0.9383 (7)	1.1993 (5)	1.1572 (3)	0.0346 (9)
O4	0.8309 (5)	1.3537 (4)	1.1160 (2)	0.0391 (7)
C5	0.8281 (7)	1.1295 (5)	1.2448 (3)	0.0356 (9)
O5	0.5886 (5)	1.0844 (4)	1.2035 (2)	0.0382 (7)
C6	0.8312 (9)	1.2552 (6)	1.3307 (3)	0.0457 (11)
O6	0.7936 (6)	1.1753 (4)	1.4246 (2)	0.0439 (8)
C7	0.6176 (9)	1.3834 (6)	1.5157 (4)	0.0509 (12)
O7	0.6520 (7)	1.5004 (5)	1.5888 (3)	0.0654 (11)
O8	0.4290 (9)	1.3564 (7)	1.4602 (4)	0.111 (2)
C8	0.8316 (8)	1.2850 (6)	1.5137 (3)	0.0451 (11)
C9	0.9055 (11)	1.1828 (7)	1.6126 (4)	0.0608 (15)

Table 2. *Selected geometric parameters (Å, °)*

C1—O1	1.402 (5)	C4—C5	1.519 (6)
C1—O5	1.421 (5)	C5—O5	1.438 (5)
C1—C2	1.525 (6)	C5—C6	1.501 (6)
O1—C10	1.423 (6)	C6—O6	1.430 (5)
C2—O2	1.424 (5)	O6—C8	1.433 (5)
C2—C3	1.516 (5)	C7—O8	1.205 (6)
C3—O3	1.421 (5)	C7—O7	1.322 (6)
C3—C4	1.520 (6)	C7—C8	1.484 (7)
C4—O4	1.446 (5)	C8—C9	1.508 (7)
O1—C1—O5	112.1 (3)	O5—C5—C6	108.0 (4)
O1—C1—C2	107.5 (3)	O5—C5—C4	110.2 (3)
O5—C1—C2	111.4 (3)	C6—C5—C4	111.0 (4)
C1—O1—C10	113.1 (4)	C1—O5—C5	113.7 (3)
O2—C2—C3	111.7 (3)	O6—C6—C5	110.0 (4)
O2—C2—C1	111.3 (3)	C6—O6—C8	112.2 (3)
C3—C2—C1	110.8 (3)	O8—C7—O7	122.8 (5)
O3—C3—C2	111.6 (3)	O8—C7—C8	124.3 (5)
O3—C3—C4	110.2 (3)	O7—C7—C8	112.8 (4)
C2—C3—C4	110.3 (3)	O6—C8—C7	110.5 (4)
O4—C4—C5	112.0 (3)	O6—C8—C9	108.3 (4)
O4—C4—C3	111.5 (3)	C7—C8—C9	112.0 (4)
C5—C4—C3	108.9 (3)		
O5—C5—C6—O6	76.4 (5)	H1—C1—O1—C10	−45.4 (3)
H8—C8—O6—C6	−34.7 (3)	O6—C8—C7—O8	10.7 (7)
C8—O6—C6—C5	170.8 (4)		

All non-H atoms were refined with anisotropic displacement parameters using a rigid-bond restraint to the U_{ij}'s of two bonded atoms (Rollett, 1970) implemented in *SHELXL*93 (Sheldrick, 1993). Floating-origin restraints are generated automatically by *SHELXL*93 (Flack & Schwarzenbach, 1988). The H atoms were positioned geometrically and allowed to ride during the least-squares refinements. Torsion-angle definitions containing H atoms are calculated with geometrically placed H atoms, thereby they are of minor significance since the e.s.d.'s of the H-atom positions are related to those of the attached atom. We also note the large anisotropy of O8 compared to the other atoms which may be the result of static disorder.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *EMACS* (Free Software Foundation, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1291). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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