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Methyl (3a*R*,4'*S*,5*R*,7*R*,7a*S*)-7-[[Cyclohexanespiro-2'-(4',5'-dihydro-2'*H*-1',3'-dioxole)]-4'-yl]-5-hydroxy-(4,5,6,7-tetrahydro-2*H*-1,3-benzodioxole)-2-spirocyclohexane-5-carboxylate

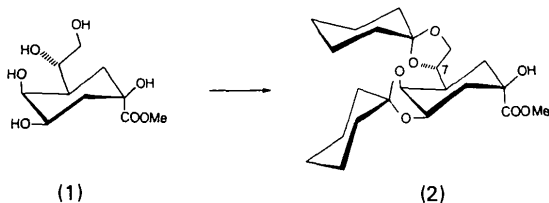
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Abstract. C₂₂H₃₄O₇, *M_r* = 410.506, monoclinic, *P*2₁, *a* = 17.550 (8), *b* = 6.196 (1), *c* = 10.181 (3) Å, β = 98.51 (3)°, *V* = 1094.9 (6) Å³, *Z* = 2, *D_x* = 1.245 (1) Mg m⁻³, λ(Cu *K*α) = 1.5406 Å, μ = 0.717 mm⁻¹, *F*(000) = 444, room temp., *R* = 0.056 for 1415 observed reflections. The chiral centre at C(7) has *S* configuration. The molecular structure shows partial disorder. The conformation of the ester side chain is stabilized by a short (C–)H...O interaction [C...O = 3.031 (7) Å]. The crystal structure is built up of infinite chains of hydrogen-bonded molecules [O...O = 2.947 (6) Å], held together by van der Waals forces.

Introduction. In the course of regio- and stereoselective synthesis of the carbocyclic analogue of 3-deoxy-β-*D*-manno-2-octulopyranosic acid (β-*KDO*) from (–)-quinic acid (Molin & Pring, 1985), ester (1) was synthesized. Its structure was established by NMR spectroscopy, but the configuration at C(7) was impossible to deduce from spectroscopic data. Therefore, (1) was converted to its dicyclohexylidene derivative (2), which could be crystallized from light petroleum, for X-ray study.



Experimental. Intensity data collected with Philips PW 1100 diffractometer, graphite-monochromatized Cu *K*α radiation, room temp., θ limit 67° (0 ≤ *h* ≤ 21, 0 ≤ *k* ≤ 8, –13 ≤ *l* ≤ 13). Intensities of 2237 reflections (sinθ/λ_{max} = 0.5971 Å⁻¹) measured from colourless needle-shaped single crystal with approximate dimensions 0.003 × 0.022 × 0.004 cm. Net intensities corrected for Lorentz and polarization effects, not for absorption. 1415 reflections with σ(*I*)/*I* < 0.33 used for refinements. Unit-cell parameters refined by least-squares fitting of cell parameters to powder pattern, taken in Guinier–Hägg-type focusing camera with strictly monochromatized Cu *K*α radiation and Si (*a* = 5.4309 Å at 298 K) as internal standard. 35 line positions with 2θ < 46.5° used in the refinement. Structure solved by direct methods, using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined on *F* by full-matrix least-squares procedure of *SHELX*76 (Sheldrick, 1976) using unit weights. Structure shows partial disorder. The O(10) atom in one of the five-membered rings (*cf.* Fig. 1) had an unusually high temperature factor, and the difference electron density calculation revealed a prominent peak in its vicinity. The two positions, this peak position O(10*B*) and the former atomic site O(10*A*), were assigned partial occupancies, which refined in the following three cycles to 0.37 and 0.63, respectively. Following this adjustment the max. and min. heights in the last difference Fourier synthesis became 0.25 and –0.20 e Å⁻³, respectively. In the last refinement, *R* = 0.056, two positions for O(10) with individual isotropic temperature factors were refined, and

no other constraints than that the sum of occupancies should be one were applied to them. The positions of the non-hydrogen atoms, except O(10), were refined with anisotropic temperature factors, hydrogen positions calculated geometrically after each cycle of refinement ($C-H = 1.08 \text{ \AA}$), except the hydroxyl H(25), which was located from difference Fourier map and held fixed during refinements. Methyl treated as a rigid group. Two group isotropic temperature factors were refined for the calculated H atoms, one for methyl hydrogens and one for remaining H positions, while H(25) had its own temperature factor refined. Four strong low- θ reflections (011, 100, 110, 210) showed large differences between F_{obs} and F_{calc} ($\Delta/\sigma > 4$), probably due to extinction, and were excluded. When the refinement was terminated, all shift/e.s.d. ratios were less than 0.14, except those of rotation parameters for the methyl group, of which the highest was 0.57. Atomic scattering factors for C and O were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), and for H atoms from Stewart, Davidson & Simpson (1965).*

The absolute configuration of the chiral centre at C(7) proved to be *S*. It could be deduced from the molecular geometry, because the present compound has four other chiral centres with known absolute configuration (Molin & Pring, 1985). Table 1 lists the final atomic coordinates, which refer to the correct enantiomer.

Discussion. Fig. 1 shows a perspective view of the molecule with the atomic labelling used. Five carbon atoms [C(12)⋯C(16)] in the cyclohexyl ring *C* have rather high temperature factors (B_{eq} range between 10.8 and 15.3 \AA^2). This is possibly a sign of structural disorder, which could not be resolved into major disorder sites, however, as for O(10) in the neighbouring ring. This disorder markedly influences the ring dimensions, which show appreciable deviations from the usual values. The remaining bond lengths and bond angles in the molecule generally conform to expected values (*cf.* Table 2).

There is a short intramolecular contact of (C)H⋯O type from the ring (C5)H atom to the carboxylic O(27) atom [$C\cdots O = 3.031(7)$, $C-H = 1.08$ (fixed), $H\cdots O = 2.29 \text{ \AA}$, $C-H\cdots O = 124^\circ$]. This type of interaction, according to Taylor & Kennard (1982), is more likely to be attractive than repulsive. Consequently, it can stabilize the molecular conformation.

* List of structure factors, anisotropic thermal parameters for C and O atoms, coordinates of calculated H atoms and intermolecular distances shorter than 3.6 \AA have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42590 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic parameters ($\times 10^4$) and equivalent isotropic/isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for the C and O atoms and for the hydroxylic H(25) atom

The e.s.d.'s, where given, are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U^\dagger
C(1)	856 (3)	849	8203 (6)	44 (2)
C(2)	651 (3)	2008 (16)	9433 (5)	42 (2)
C(3)	1094 (3)	4109 (15)	9761 (5)	45 (2)
C(4)	1961 (3)	3823 (15)	9789 (5)	44 (2)
C(5)	2215 (3)	2392 (16)	8709 (6)	49 (2)
C(6)	1718 (3)	377 (15)	8402 (6)	48 (2)
C(7)	3079 (3)	1921 (17)	9046 (7)	63 (3)
O(8)	3343 (3)	924 (16)	7938 (5)	79 (2)
C(9)	3939 (5)	-531 (22)	8433 (10)	96 (4)
O(10A)	3620 (7)	-1580 (23)	9498 (10)	97 (5)
O(10B)	4067 (11)	-443 (37)	9891 (17)	93 (8)
C(11)	3330 (4)	283 (19)	10161 (8)	76 (4)
C(12)	3886 (6)	-2446 (26)	7439 (13)	149 (7)
C(13)	4212 (6)	-2127 (29)	6371 (12)	167 (8)
C(14)	4999 (6)	-1160 (25)	6543 (10)	138 (6)
C(15)	4995 (7)	749 (30)	7442 (14)	194 (9)
C(16)	4704 (5)	578 (27)	8488 (12)	161 (7)
O(17)	1045 (2)	4696 (13)	11116 (4)	48 (1)
C(18)	1748 (3)	4068 (16)	11959 (6)	49 (2)
O(19)	2184 (2)	2936 (13)	11089 (4)	46 (1)
C(20)	1573 (3)	2509 (16)	13009 (6)	51 (2)
C(21)	2308 (4)	1912 (18)	13966 (7)	69 (3)
C(22)	2690 (4)	3944 (18)	14591 (7)	74 (3)
C(23)	2874 (4)	5483 (19)	13501 (7)	76 (3)
C(24)	2152 (4)	6080 (16)	12519 (7)	61 (3)
O(25)	469 (2)	-1192 (12)	8078 (4)	50 (2)
C(26)	591 (4)	2171 (16)	6941 (6)	49 (2)
O(27)	1002 (3)	3078 (16)	6299 (5)	91 (3)
O(28)	-167 (2)	2118 (14)	6636 (4)	67 (2)
C(29)	-507 (4)	3190 (19)	5429 (4)	77 (3)
H(25)	-35	-865	8126	91 (27)

$$\dagger U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

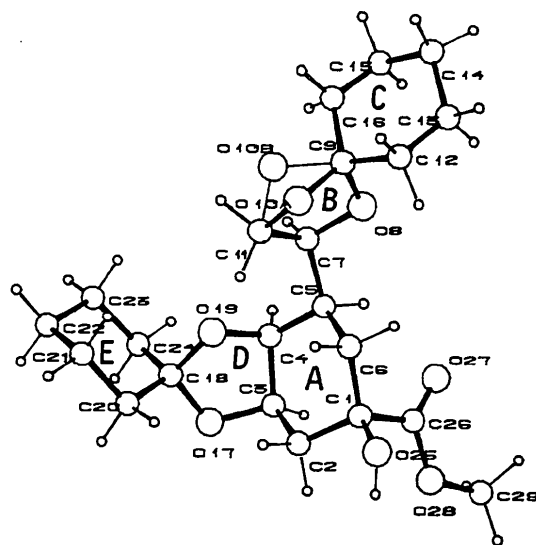


Fig. 1. View of the title molecule with atoms numbered as in the text. In the ring *B* atom O(10) has two major disorder sites with the partial occupancies 0.63 [O(10A)] and 0.37 [O(10B)], respectively.

The cyclohexyl rings *A* and *C* show a more or less distorted (flattened) chair conformation (the r.m.s. torsion angles are 49.1 and 43.1°, respectively), while ring *E* is almost an ideal chair (the r.m.s. torsion angle is 55.7°). The calculated ring puckering parameters, according to Cremer & Pople (1975), are shown in Table 3. In the five-membered ring *B*, atom O(10) has two different positions. The ring conformation is

Table 2. Intramolecular bond lengths (Å) and bond angles (°) between the C and O atoms (with e.s.d.'s in parentheses)

C(1)–C(2)	1.532 (8)	O(10B)–C(11)	1.434 (22)
C(1)–C(6)	1.525 (8)	O(10A)–C(11)	1.466 (17)
C(1)–O(25)	1.432 (7)	C(12)–C(13)	1.317 (18)
C(1)–C(26)	1.537 (8)	C(13)–C(14)	1.492 (16)
C(2)–C(3)	1.528 (12)	C(14)–C(15)	1.496 (22)
C(3)–C(4)	1.529 (8)	C(15)–C(16)	1.251 (19)
C(3)–O(17)	1.441 (7)	O(17)–C(18)	1.448 (7)
C(4)–C(5)	1.529 (10)	C(18)–O(19)	1.437 (9)
C(4)–O(19)	1.433 (8)	C(18)–C(20)	1.505 (11)
C(5)–C(6)	1.528 (12)	C(18)–C(24)	1.504 (12)
C(5)–C(7)	1.533 (8)	C(20)–C(21)	1.541 (9)
C(7)–O(8)	1.423 (10)	C(21)–C(22)	1.521 (14)
C(7)–C(11)	1.537 (13)	C(22)–C(23)	1.533 (13)
O(8)–C(9)	1.416 (13)	C(23)–C(24)	1.538 (10)
C(9)–O(10A)	1.446 (16)	C(26)–O(27)	1.185 (10)
C(9)–O(10B)	1.469 (20)	C(26)–O(28)	1.321 (7)
C(9)–C(12)	1.552 (19)	O(28)–C(29)	1.445 (10)
C(9)–C(16)	1.502 (15)		

O(25)–C(1)–C(26)	108.4 (3)	O(10A)–C(9)–C(16)	128.3 (9)
C(6)–C(1)–C(26)	112.6 (5)	O(10A)–C(9)–C(12)	98.8 (10)
C(6)–C(1)–O(25)	106.9 (4)	C(9)–O(10A)–C(11)	101.0 (10)
C(2)–C(1)–C(26)	110.8 (4)	C(9)–O(10B)–C(11)	101.4 (12)
C(2)–C(1)–O(25)	108.7 (3)	C(7)–C(11)–O(10B)	103.5 (9)
C(2)–C(1)–C(6)	109.3 (3)	C(7)–C(11)–O(10A)	105.1 (7)
C(1)–C(2)–C(3)	113.8 (4)	C(9)–C(12)–C(13)	115.6 (13)
C(2)–C(3)–O(17)	108.9 (5)	C(12)–C(13)–C(14)	118.2 (11)
C(2)–C(3)–C(4)	112.2 (7)	C(13)–C(14)–C(15)	107.5 (10)
C(4)–C(3)–O(17)	102.2 (4)	C(14)–C(15)–C(16)	119.6 (15)
C(3)–C(4)–O(19)	101.3 (4)	C(9)–C(16)–C(15)	118.8 (11)
C(3)–C(4)–C(5)	116.7 (5)	C(3)–O(17)–C(18)	109.5 (4)
C(5)–C(4)–O(19)	111.9 (6)	O(17)–C(18)–C(24)	108.3 (6)
C(4)–C(5)–C(7)	109.4 (5)	O(17)–C(18)–C(20)	110.4 (5)
C(4)–C(5)–C(6)	113.8 (5)	O(17)–C(18)–O(19)	104.5 (4)
C(6)–C(5)–C(7)	113.9 (7)	C(20)–C(18)–C(24)	113.4 (5)
C(1)–C(6)–C(5)	113.3 (5)	O(19)–C(18)–C(24)	111.9 (5)
C(5)–C(7)–C(11)	117.2 (6)	O(19)–C(18)–C(20)	107.9 (6)
C(5)–C(7)–O(8)	109.4 (5)	C(4)–O(19)–C(18)	106.6 (5)
O(8)–C(7)–C(11)	102.0 (6)	C(18)–C(20)–C(21)	111.3 (5)
C(7)–O(8)–C(9)	107.7 (6)	C(20)–C(21)–C(22)	110.0 (7)
O(8)–C(9)–C(16)	109.3 (10)	C(21)–C(22)–C(23)	109.8 (6)
O(8)–C(9)–C(12)	106.5 (8)	C(22)–C(23)–C(24)	112.3 (6)
O(8)–C(9)–O(10B)	109.3 (10)	C(18)–C(24)–C(23)	110.1 (8)
O(8)–C(9)–O(10A)	101.9 (8)	C(1)–C(26)–O(28)	110.7 (5)
C(12)–C(9)–C(16)	110.0 (9)	C(1)–C(26)–O(27)	125.5 (5)
O(10B)–C(9)–C(16)	86.7 (10)	O(27)–C(26)–O(28)	123.8 (6)
O(10B)–C(9)–C(12)	132.2 (13)	C(26)–O(28)–C(29)	117.6 (5)

Table 3. Ring puckering parameters (with e.s.d.'s in parentheses) calculated according to Cremer & Pople (1975)

Ring	Q(Å)	φ(°)	θ(°)
A	0.51 (1)	–174 (3)	166 (1)
B*	0.43 (1)	81 (1)	
B†	0.38 (1)	–37 (2)	
C	0.40 (1)	164 (13)	10 (2)
D	0.37 (1)	173 (1)	
E	0.57 (1)	154 (12)	4 (1)

* With atom O(10A) as a ring atom.

† With atom O(10B) as a ring atom.

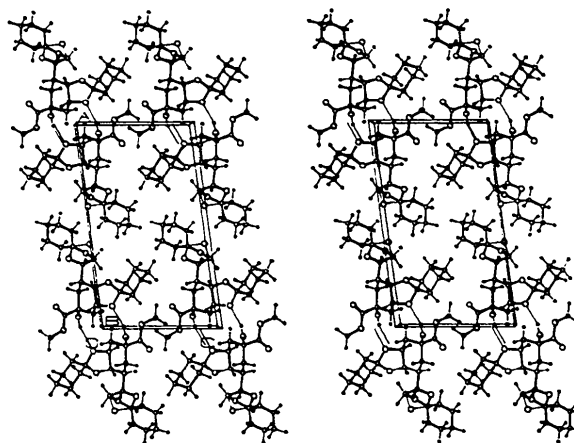


Fig. 2. Stereoscopic packing diagram of the crystal structure.

intermediate between envelope and half-chair with O(10A) and 'near-envelope' with O(10B) as a ring atom. Ring *D* is also intermediate between envelope and half-chair (*cf.* Table 3).

In the crystal structure, molecules related by the symmetry operation $-x, \pm 0.5+y, 2-z$ are linked together by hydrogen bonds between the hydroxylic (O25)H and the ring O(17) atom [O...O = 2.947 (6), O–H = 0.92, H...O = 2.06 Å, O–H...O = 161°]. This bonding also leads to short intermolecular distances from O(17) to C(2) [3.28 (1) Å] and O(28) [3.30 (1) Å]. All the other intermolecular contacts have lengths expected for van der Waals distances. Fig. 2 is a packing diagram.

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