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1-*N*,2-*O*-Carbonyl-3,5-*O*-isopropylidene-1-*N*-[(2*R*)-2-methyl-3-oxopentanoyl]- α -*D*-xylofuranosylamine

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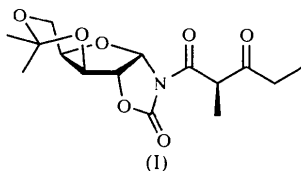
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Abstract

The title compound, C₁₅H₂₁NO₇, was synthesized as part of a study involving the testing of new carbohydrate-derived chiral auxiliaries. Its solid-state conformation and absolute configuration were determined. The *R* configuration for the chiral centre at C-22, created during the synthesis, was deduced from knowledge of the absolute structure of the *D*-xylose moiety.

Comment

During the course of our studies of the efficiency of *D*-xylose-based chiral oxazolidin-2-ones in stereoselective reactions, we investigated α -acylation reactions. The title compound, 1-*N*,2-*O*-carbonyl-3,5-*O*-isopropylidene-1-*N*-[(2*R*)-2-methyl-3-oxopentanoyl]- α -*D*-xylofuranosylamine, (I), was obtained by propionylation of the *N*-propionyl derivative of the chiral auxiliary (Köll & Lützen, 1997). It was also obtained as an undesired by-product when we tried to react the *N*-propionyl derivative of the auxiliary with less reactive alkyl halides (Köll & Lützen, 1996).



In order to prove the proposed mechanism (Evans *et al.*, 1981, Köll & Lützen, 1997), we have determined unambiguously the absolute stereochemistry of the newly formed chiral centre at C-22. Since the absolute stereochemistry of the *D*-xylose-based moiety is known, the configuration of C-22 could be assigned as *R*; this was further substantiated by the Flack parameter [$\chi = 0.02(18)$; Flack, 1983].

The tricyclic molecule (Fig. 1) adopts an expected staircase-like conformation with the furanoid ring in a ³T₄ conformation [Cremer–Pople puckering parameters:

$Q = 0.349(2) \text{ \AA}$ and $\Phi = 313.6(3)^\circ$ (Cremer & Pople, 1975)] in the centre. The annelated oxazolidin-2-one ring with its carbamate function is, unsurprisingly, found in an almost planar conformation [puckering parameters: $Q = 0.078(2) \text{ \AA}$ and $\Phi = 238.2(13)^\circ$]. The six-membered acetal-containing ring on the other side adopts an almost ideal chair conformation [puckering parameters: $Q = 0.499(2) \text{ \AA}$, $\Theta = 172.0(2)^\circ$ and $\Phi = 122.3(15)^\circ$].

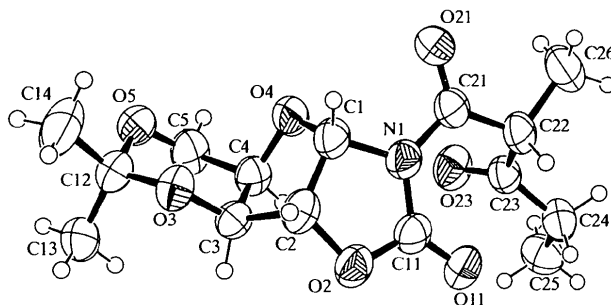


Fig. 1. ORTEP (Burnett & Johnson, 1996) drawing of (I) showing displacement ellipsoids at 50% probability and the atomic numbering scheme.

The crystal structure shows five inter- and one intramolecular non-classical C—H...O hydrogen bonds (Jeffrey *et al.*, 1985), details of which are given in Table 1. Whereas the H...O distances of most of these hydrogen bonds are in the normal range between 2.5 and 2.6 Å, the intermolecular distance between H2 and O21 is only 2.338(2) Å, indicating much stronger hydrogen bonding (Steiner, 1996).

Experimental

Adapting a protocol by Evans *et al.* (1981), 1-*N*,2-*O*-carbonyl-3,5-*O*-isopropylidene-*N*-propionyl- α -*D*-xylofuranosylamine, (2), was converted into the lithium enolate using lithium bis(trimethylsilyl)amide (LiHMDS) as base. In a second step, a 1.6-fold excess of propionyl chloride was added to a solution of the enolate in tetrahydrofuran at 195 K. The title compound, (I), was obtained in 45% yield after column chromatography. Suitable crystals (m.p. 409 K) were obtained from a mixture of dichloromethane and petroleum ether upon slow evaporation.

Crystal data

C₁₅H₂₁NO₇
M_r = 327.33
 Orthorhombic
*P*2₁2₁2₁
a = 9.201(1) Å
b = 10.027(1) Å
c = 18.217(2) Å
V = 1680.7(3) Å³
Z = 4
D_x = 1.294 Mg m⁻³
D_m not measured

Cu *K* α radiation
 λ = 1.54178 Å
 Cell parameters from 25 reflections
 θ = 42.1–46.5°
 μ = 0.872 mm⁻¹
T = 293(2) K
 Block
 0.50 × 0.40 × 0.40 mm
 Colourless

Data collection

Enraf–Nonius CAD-4
diffractometer
2 θ/ω scans
Absorption correction: none
3850 measured reflections
2033 independent reflections
(plus 1259 Friedel-related reflections)
3120 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 76.47^\circ$
 $h = -11 \rightarrow 11$
 $k = -12 \rightarrow 12$
 $l = -22 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.103$
 $S = 1.075$
3292 reflections
234 parameters
H atoms treated by a
mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.1628P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.089$

$\Delta\rho_{\text{max}} = 0.141 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.148 \text{ e } \text{\AA}^{-3}$
Extinction correction:
SHELXL97
Extinction coefficient:
0.0053 (5)
Scattering factors from
*International Tables for
Crystallography* (Vol. C)
Absolute structure:
Flack (1983)
Flack parameter = 0.02 (18)

Table 1. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
C2—H2...O21 ⁱ	0.98	2.34	3.199 (2)	146
C22—H22...O5 ⁱⁱ	0.98	2.58	3.516 (2)	160
C22—H22...O11	0.98	2.51	2.848 (2)	100
C13—H133...O11 ⁱⁱⁱ	0.96	2.49	3.424 (2)	164
C24—H242...O23 ^{iv}	0.97	2.59	3.543 (2)	170
C25—H252...O4 ^{iv}	0.96	2.58	3.410 (2)	145

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

Friedel opposites were collected, were regarded as symmetry independent and were thus not merged. The absolute structure was also determined by refinement of the Flack enantiomorph parameter (χ) which refined to 0.02 (18) (Flack, 1983). H atoms were included using a riding model (*SHELXL97*; Sheldrick, 1997), but their displacement parameters were refined freely; rigid methyl groups were allowed to rotate but not tip, thus contributing one additional parameter each.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *CAD-SHEL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Burnett & Johnson, 1996). Software used to prepare material for publication: *PLATON96* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1359). Services for accessing these data are described at the back of the journal.

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1,4,7,10-Tetraoxacyclododecane–acetone thiosemicarbazone (1/2)

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Abstract

In the centrosymmetric formula unit of the title complex, C₈H₁₆O₄·2C₄H₉N₃S, the 1,4,7,10-tetraoxacyclododecane molecule adopts the biangular [66] conformation and the thiosemicarbazone molecules are linked to the macrocycle *via* a long and appreciably bent N—N—H...O hydrogen bond [N...O 2.992 (2) Å and N—H...O 158 (2)°]. These units are associated into sheets by two additional hydrogen bonds, N—H...O and N—H...S, originating from the NH₂ group and utilizing the thioureido S atom or the second crystallographically independent ether O atom as acceptors.

Comment

According to a search of the October 1998 version of the Cambridge Structural Database (Allen & Kennard, 1993), the number of metal-free crystal structures in which 1,4,7,10-tetraoxacyclododecane (12-crown-4) has been found to interact directly with uncharged mol-