Software used to prepare material for publication: *XL* in *SHELXTL/PC*.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: CR1168). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Comment

In the course of synthetic studies towards *trans,trans-N-*(1-carboxyethyl)-3,5-dihydroxy-4-acetamidopiperidine, a key step was the stereospecific incorporation of the *N*-acetyl moiety. We devised a synthetic route to the diacetate (2) (see scheme below).

(1)   (2)

While ^{1}H NMR and mass spectroscopic data indicated (2) to be a single diastereomer, assignment of the absolute stereochemistry by ^{1}H NMR methods was not possible. This was due to the uncertainty of relating scalar coupling constants to torsion angles in the furanosyl rings. Furthermore, because of the similar chemical shifts of the relevant proton signals, irradiation of a single signal alone, required for NOE difference experiments, was not possible. The crystal structure was, therefore, determined in order to ascertain the stereochemistry of the title compound, (2).

The displacement ellipsoid drawing of (2) with the atom-labeling scheme is given in Fig. 1. The absolute configuration of (2) was assigned from knowledge of the stereochemistry of its synthetic precursor. Molecules of (2) comprise two heterocyclic five-membered rings [*A* (furanose) and *B* (dioxolane)] *cis*-fused along the C1—C2 bond. Both rings adopt envelope conformations

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3-Acetamido-5-*O*-acetyl-1,2-*O*-isopropyl-idene-D-ribofuranose

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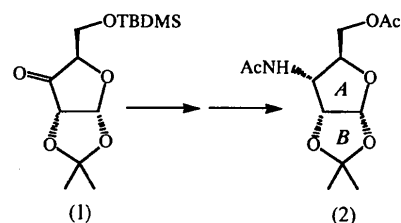
Abstract

The crystal structure of the title compound, $C_{12}H_{19}NO_6$, was determined in order to ascertain its relative configuration. It was synthesized by the stereospecific reduction of the novel oxime derived from 5-*O*-acetyl-1,2-isopropylidene-3-oxo-α-D-ribofuranose and comprises two *cis*-fused heterocyclic five-membered rings, furanose and dioxolane, which adopt envelope conformations.
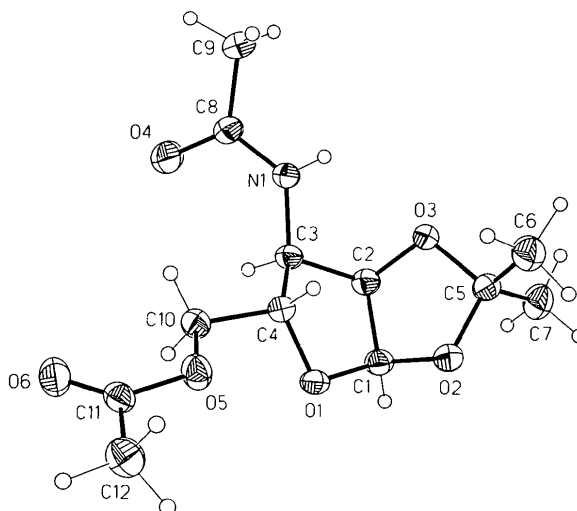
Fig. 1. The molecular structure of (2), with 50% probability ellipsoids, showing the atom-numbering scheme. The carbonyl O atom is disordered over two positions, O4 and O4', with occupancies of 0.63 (5) and 0.37 (5), respectively. H atoms are shown as small circles of arbitrary radii.

[E^4 and E^5 for *A* and *B*, respectively]. Atoms C4 and C5 occupy the flap positions and are at $-0.589\,(2)$ and $0.403\,(2)$ Å from their respective envelope planes (O1, C1, C2, C3 and O2, C2, C3, O3). The fused-ring system is folded and has a dihedral angle of $116.2\,(1)^\circ$ between the ring envelope planes, with the flap of ring *A* lying inside this fold and the flap of ring *B* outside the fold. Angles of $140.3\,(1)$ and $152.5\,(2)^\circ$ are observed between the envelope plane and flap for *A* and *B*, respectively. A search of the October 1995 release of the Cambridge Structural Database (Allen *et al.*, 1991) using a fragment made up of the bicyclic ring system and first-atom substituents on C3 and C5 yielded three hits. The refcodes for these three structures are AEPIDF (Brimacombe, Iball & Low, 1972), JUFMOM (Tronchet, Koufaki, Zosimo-Landolfo & Bernardinelli, 1992) and VUJDEJ (Tronchet, Jean, Barbalat-Rey & Bernardinelli, 1992). While AEPIDF has the same ring conformations as (2), JUFMOM has ring *A* in the $^1T_4$ twist conformation and ring *B* in VUJDEJ has the $^2T_5$ twist conformation. The conformation around the C4—C10 bond is *gauche*, with the O1—C4—C10—O5 torsion angle being $70.6\,(2)^\circ$.

Experimental

Compound (1) was obtained from 1,2-isopropylidene-D-furanose (Aldrich) in two steps by protection of the 5-OH group with *tert*-butyldimethylsilyl chloride, followed by oxidation of the 3-OH group with DMSO/oxalyl chloride/triethylamine. Compound (2) was obtained from compound (1) by the following sequence: treatment of (1) with hydroxylamine hydrochloride/sodium acetate in methanol afforded the oxime, and then reduction of the oxime (lithium aluminium hydride, THF) and acetylation (acetic anhydride/pyridine) provided compound (2). Colorless plates of (2) were obtained by slow evaporation from a CH_2Cl_2 solution.

Crystal data

$C_{12}H_{19}NO_6$
$M_r = 273.28$
Orthorhombic
$P2_12_12_1$
$a = 8.7563\,(1)$ Å
$b = 9.0187\,(2)$ Å
$c = 16.9354\,(4)$ Å
$V = 1337.40\,(4)$ Å^3
$Z = 4$
$D_x = 1.357$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3997 reflections
$\theta = 3-27^\circ$
$\mu = 0.109$ mm^{-1}
$T = 173\,(2)$ K
Plate
$0.22 \times 0.17 \times 0.14$ mm
Colorless

Data collection

SMART Platform diffractometer
ω scans
Absorption correction: none
4751 measured reflections
2342 independent reflections
2236 reflections with $I > 2\sigma(I)$

$R_{int} = 0.0345$
$\theta_{max} = 27.06^\circ$
$h = -11 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -21 \rightarrow 7$
Intensity decay: $< 1\%$

Refinement

Refinement on F^2
$R(F) = 0.0305$
$wR(F^2) = 0.0932$
$S = 1.092$
2340 reflections
259 parameters
H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 0.3927P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.175$ e Å^{-3}
$\Delta\rho_{min} = -0.141$ e Å^{-3}
Extinction correction: SHELXTL
Extinction coefficient: 0.035\,(3)
Scattering factors from International Tables for Crystallography (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.0\,(9)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.410 (2)	N1—C8	1.346 (2)
O1—C4	1.442 (2)	N1—C3	1.442 (2)
O2—C1	1.415 (2)	C1—C2	1.539 (2)
O2—C5	1.428 (2)	C2—C3	1.536 (2)
O3—C2	1.426 (2)	C3—C4	1.537 (2)
O3—C5	1.434 (2)		
C1—O1—C4	107.16 (11)	O3—C2—C3	109.74 (14)
C1—O2—C5	109.07 (13)	O3—C2—C1	104.86 (15)
C2—O3—C5	108.12 (12)	C3—C2—C1	104.25 (12)
C8—N1—C3	124.6 (2)	N1—C3—C2	112.36 (13)
O1—C1—O2	110.13 (14)	N1—C3—C4	113.82 (14)
O1—C1—C2	107.24 (13)	C2—C3—C4	101.28 (13)
O2—C1—C2	104.91 (13)	O1—C4—C3	103.41 (13)

The carbonyl O atom was disordered and was refined over two positions, O4 and O4'. Their occupancy factors were refined to 0.63\,(5) for O4 and 0.37\,(5) for O4'. The Flack (1983) parameter refined to a value of 0.03\,(93), its large error rendering it indeterminate as to the absolute configuration of the title compound, whose configuration is known from the stereochemistry of the starting material.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SMART* and *SAINT* (Siemens, 1994*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Bis[(S)-(−)-α-methylbenzyl]thiourea

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Abstract

The title compound, 1,3-bis[(*S*)-(−)-1-phenylethyl]thiourea, $C_{17}H_{20}N_2S$, exhibits bond lengths and angles consistent with the build-up of negative charge on the S atom. There are weak hydrogen bonds between molecules leading to helices disposed about crystallographic 3_1 axes.

Comment

Our recent interest in the application of guanidines as ligands for transition metals has lead us to isolate a number of different thiourea compounds as intermediates in their synthesis (Bailey, Blake, Kryszczuk, Parsons & Reed, 1995). We report here the crystal structure of one of these, namely, enantiomerically pure bis[(*S*)-(−)-α-methylbenzyl]thiourea, (1), which was synthesized *via* standard procedures from (*S*)-(−)-α-methylbenzylamine and carbon disulfide (Yamazaki, Higashi & Iguchi, 1974).

(1)
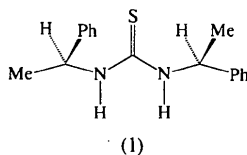
The crystal structure is composed of discrete molecules of (1) (Fig. 1), the bond lengths and angles (Table 1) being quite typical for acyclic thiourea compounds in the Cambridge Structural Database (Allen & Kennard, 1993; Fletcher, McMeeking & Parkin,
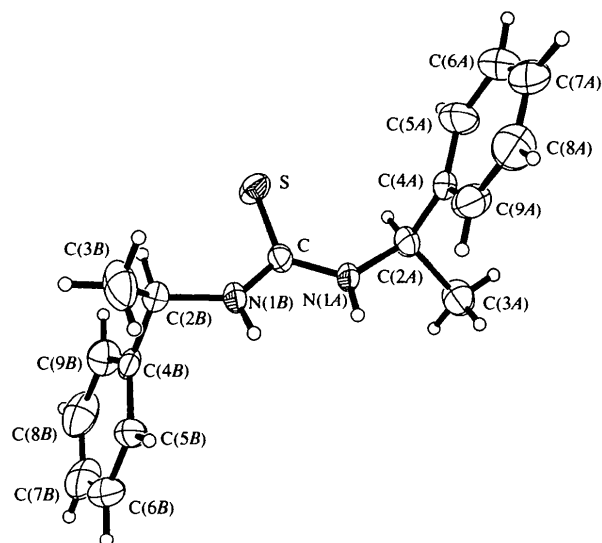

Fig. 1. A view of the title molecule with the atom-numbering scheme. Displacement ellipsoids enclose 30% probability surfaces. The dihedral angle between the planes of the phenyl rings is 11.6 (4)°.

1996). The C—S bond length [1.710 (7) Å] lies at the low end of the range associated with C—S single bonds (1.70–1.80 Å; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1992), while the average C—N bond length [1.321 (8) Å] is similar to 'standard' C—N bonds in aromatic rings [1.336 (14) Å; Allen *et al.*, 1992]. Compound (1) should thus be properly regarded as a resonance hybrid of C=N-containing canonical forms, with only a relatively small contribution from the C=S-bonded form frequently used to represent thiourea compounds (see scheme below). The phenyl groups adopt a pseudo-antiperiplanar arrangement in order to minimize steric crowding of the α-methylbenzyl functionality.

R = —CH(Me)Ph
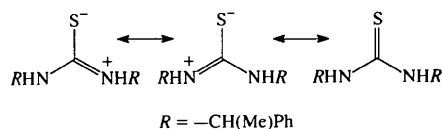
Hydrogen bonds link molecules to form a helix around the crystallographic threefold screw axis. Each molecule is linked to its neighbour in the helix by two N—H···S interactions [N1A···S^i 3.411 (6) and N1B···S^i 3.545 (7) Å; symmetry code: (i) $2 - y$, $1 + x - y$, $\frac{1}{3} + z$]. There appear to be no significant contacts between the helices.

Experimental

Crystals of (1) were grown from dichloromethane layered with diethyl ether. At 1.08 mm, the crystal selected for study is long by normal standards, but the crystals shattered when attempts were made to cut them. A 1.2 mm diameter collimator was used during data collection.