

$S = 1.098$
3411 reflections
183 parameters
H atoms in calculated
positions, but not refined

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.623 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.958 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

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Table 1. Selected geometric parameters (Å, °)

C1—O14	1.441 (5)	C8—O14	1.445 (5)
C1—C2	1.520 (7)	C8—C9	1.540 (6)
C1—C13	1.554 (6)	C9—C10	1.519 (6)
C2—C3	1.556 (6)	C9—C13	1.556 (6)
C2—C7	1.562 (6)	C9—Br9	1.925 (4)
C3—O15	1.439 (6)	C10—O10	1.207 (6)
C3—C4	1.505 (7)	C10—N11	1.366 (7)
C4—C5	1.317 (8)	N11—C12	1.372 (7)
C5—C6	1.518 (7)	N11—C11	1.468 (7)
C6—O15	1.437 (6)	C12—O12	1.209 (6)
C6—C7	1.559 (6)	C12—C13	1.506 (7)
C7—C8	1.521 (6)	C13—Br13	1.926 (4)
O14—C1—C2	104.6 (3)	O10—C10—N11	124.8 (5)
C4—C5—C6	105.4 (5)	O10—C10—C9	126.6 (5)
O15—C6—C5	101.7 (4)	N11—C10—C9	108.6 (4)
O15—C6—C7	102.2 (4)	C10—N11—C12	113.9 (4)
C5—C6—C7	104.9 (4)	C10—N11—C11	121.9 (5)
C8—C7—C6	115.5 (4)	C12—N11—C11	124.2 (5)
C8—C7—C2	101.8 (4)	O12—C12—N11	124.2 (5)
C6—C7—C2	100.5 (3)	O12—C12—C13	126.5 (5)
O14—C8—C7	104.4 (3)	N11—C12—C13	109.2 (4)
O14—C8—C9	99.0 (3)	C12—C13—C1	111.0 (4)
C7—C8—C9	110.6 (3)	C12—C13—C9	104.0 (4)
C10—C9—C8	110.2 (4)	C1—C13—C9	101.1 (3)
C10—C9—C13	104.3 (4)	C12—C13—Br13	107.5 (3)
C8—C9—C13	101.6 (3)	C1—C13—Br13	114.3 (3)
C10—C9—Br9	107.0 (3)	C9—C13—Br13	118.5 (3)
C8—C9—Br9	114.5 (3)	C1—O14—C8	97.1 (3)
C13—C9—Br9	118.7 (3)	C6—O15—C3	95.9 (3)

Data collection: *SDP-Plus* (Frenz, 1985). Cell refinement: *SDP-Plus*. Data reduction: *Xtal3.2 DIFDAT* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLATON96* (Spek, 1996). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1163). Services for accessing these data are described at the back of the journal.

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(1*R*,2*R*)-4-Methylurazole- α -D-pyranosyl-2-deoxyriboside from Reaction of 4-Methylurazole with 2-Deoxy-D-ribose

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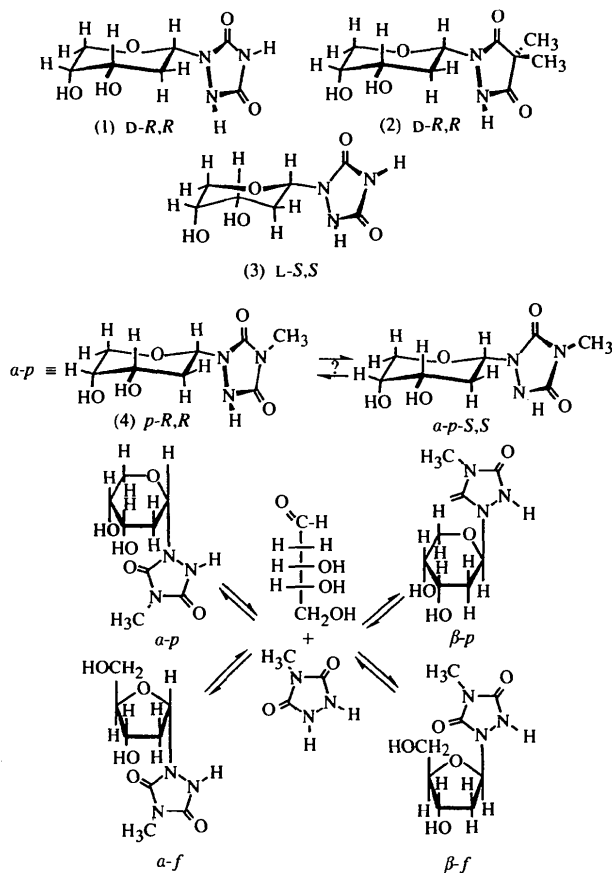
Abstract

The crystalline nucleoside formed from an aqueous solution of 4-methylurazole and 2-deoxy-D-ribose was identified unequivocally by its X-ray structure as a single diastereomer, (1*R*,2*R*)-4-methylurazole- α -D-pyranosyl-2-deoxyriboside [IUPAC name: (1*R*,2*R*)-1-(2-deoxy- α -D-erythro-pentopyranosyl)-4-methyl-1,2,4-triazolidine-3,5-dione; C₈H₁₃N₃O₅]. In its urazole ring, the two hydrazidic N atoms are pyramidal and confer *R* chirality, the respective pyranosyl and H-atom substituents being substantially out of the ring plane and *trans* juxtaposed, while the imidic N atom is trigonal planar, its methyl substituent being essentially coplanar with the ring. The intermolecular hydrogen bonding involves pyranose–pyranose and pyranose–urazole interactions producing one-dimensional cross-linked double chains. From this study and our results from the preparation of three related nucleosides, we find that the crystalline nucleosides formed by direct coupling of these nucleobases with 2-deoxyribose are consistently diastereospecific.

Comment

Our studies of the crystalline structures of 1-methylurazole, 4-methylurazole and 1,2,4-trimethylurazole showed them to be racemic molecules (Meyers, Lutfi, Hou & Robinson, 1995, 1997; Meyers, Lutfi, Kolb & Robinson, 1994). While their imidic N4 atoms are trig-

onal planar, their hydrazidic N1 and N2 atoms are pyramidal with their substituents *trans* juxtaposed, giving the molecules *R,R* and *S,S* chiralities. These results were consistent, whether there were substantial differences in the intermolecular hydrogen-bonding patterns or even no hydrogen bonding (*viz.* trimethylurazole). It was surprising to find, therefore, that the nucleosides prepared from the reaction of 2-deoxy-D-ribose with urazole (Robinson, Meyers, Kolb & Colloton, 1996) and with the related 4,4-dimethylpyrazolidine-3,5-dione (Kolb, Colloton, Robinson, Lutfi & Meyers, 1996) were the single diastereomers (1) and (2), respectively, their nitrogen-containing rings having *R,R* chirality associated with the pyramidal hydrazidic N atoms. Diastereomeric specificity of these reactions was supported by our recent identification of the nucleoside formed in the reaction of 2-deoxy-L-ribose with urazole as a single diastereomer (3), the urazole moiety of which possessed *S,S* chirality (Robinson, Kolb, Colloton & Meyers, 1997). To broaden the spectrum of the correlation, the reaction of 2-deoxy-D-ribose with 4-methylurazole was carried out. As shown in the scheme, the α - and β -furanosides (α -*f* and β -*f*) and corresponding pyranosides (α -*p* and β -*p*) could be expected products. The resultant crystals were isolated and examined by X-ray diffraction.



The X-ray structure determination identified the crystals as the single diastereomer (1*R*,2*R*)-4-methylurazole- α -D-pyranosyl-2-deoxyribose, (4), the absolute configuration being ascertained from the known configuration of the D-2-deoxyribose moiety. Fig. 1 shows its molecular structure with atom numbering and displacement ellipsoids. The urazole ring of crystalline (4) is essentially planar, the mean deviation from the plane being 0.045 (3) Å. The *R,R* chirality derives from the pyramidal hydrazidic N1 and N2 atoms and the *trans* juxtaposition of C1' of the pyranosyl ring and H2, which imposes torsion angles of -67 (2) for C1'—N1—N2—H2, -144.8 (2) for C1'—N1—C5—N4 and -152 (3)° for H2—N2—C3—N4. The pyramidal disposition of N1 is further illustrated by the torsion angle of 150.8 (2)° for C1'—N1—N2—C3. The trigonality of the imidic N4 atom is consistent with the ring—C8 coplanarity, the torsion angles being -177.7 (3) for C8—N4—C3—N2 and -174.7 (3)° for C8—N4—C5—N1. Full resonance involving the imidic N4 atom with both C=O groups is readily effected by the coplanarity of O6—C5—N4—C3—O7, with torsion angles of -179.5 (3) for O6—C5—N4—C3 and -173.8 (3)° for O7—C3—N4—C5. The overall geometric parameters and chiral aspects of crystalline (4) are very similar to those we reported for (1*R*,2*R*)-urazole- α -D-pyranosyl-2-deoxyribose, (1) (Robinson *et al.*, 1996), (1*R*,2*R*)-4,4-dimethylpyrazolidine-3,5-dione- α -D-pyranosyl-2-deoxyribose, (2) (Kolb *et al.*, 1996), and (1*S*,2*S*)-urazole- α -L-pyranosyl-2-deoxyribose, (3) (Robinson *et al.*, 1997). Likewise, the parameters and chiral aspects of the urazole moiety of crystalline (4) closely resemble those we found for the (1*R*,2*R*) and (1*S*,2*S*) enantiomers of 1,2,4-trimethylurazole, 1-methylurazole and 4-methylurazole in their respective racemic mixtures (Meyers *et al.*, 1997, 1994, 1995; *cf.* Tenon, Carles & Aycard, 1995; Belaj, 1992; Baker, Timberlake, Alender, Majeste & Trefonas, 1982).

The data in Table 1 show that intermolecular hydrogen bonding involves pyranose—pyranose and pyranose—urazole interactions which produce cross-linked double

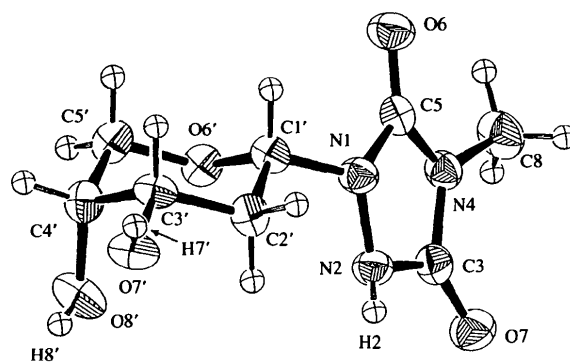


Fig. 1. Molecular structure and atom-numbering scheme of (4) with displacement ellipsoids at the 50% probability level.

chains, as illustrated in Fig. 2. Each molecule is linked *via* six hydrogen bonds to four surrounding molecules in which the urazole hydrazidic N2 atom is a donor and the adjacent carbonyl O7 atom is an acceptor, while the pyranose hydroxylic O7' and O8' atoms are donors as well as acceptors. The O6' atom in the pyranose ring does not participate in hydrogen bonding with N—H or O—H, a situation we also noted for (1) (Robinson *et al.*, 1996), (2) (Kolb *et al.*, 1996) and (3) (Robinson *et al.*, 1997), and that has been reported for ribofuranosides (Birnbbaum, Blonski & Hruska, 1983). While the hydrazidic N1, imidic N4 and carbonyl O6 atoms of the urazole are not involved in hydrogen bonding here in the usual sense, the possibility of a weak C5'—H5'a···O6 intermolecular interaction was detected (*cf.* Glusker, Lewis & Rossi, 1994).

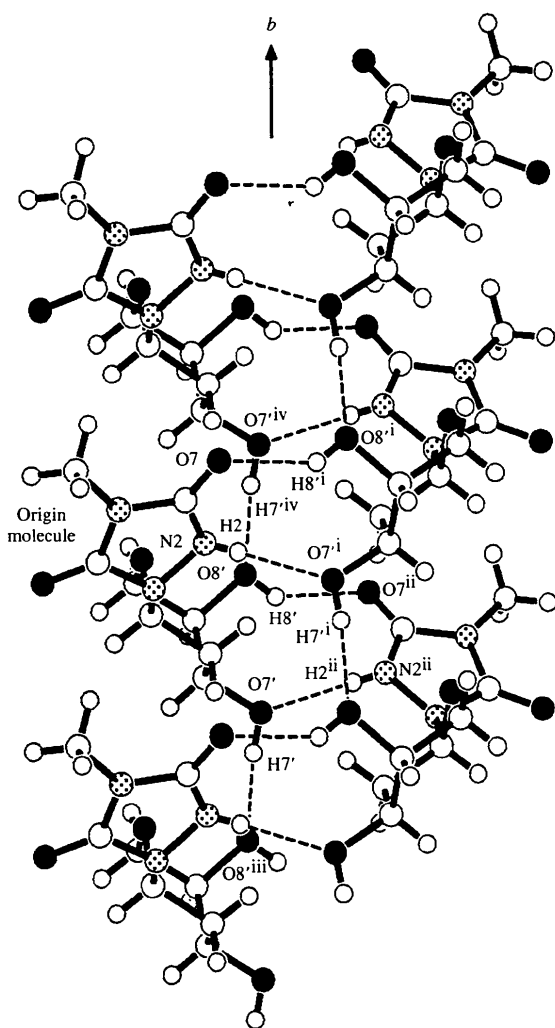


Fig. 2. Linear cross-linked hydrogen-bonding scheme of (4). The origin molecule is hydrogen bonded to four adjacent molecules *via* six hydrogen bonds. Symmetry codes: (i) $1 - x, y + \frac{1}{2}, -z$; (ii) $1 - x, y - \frac{1}{2}, -z$; (iii) $x, y - 1, z$; (iv) $x, y + 1, z$.

The intermolecular hydrogen bonding and one-dimensional cross-linked double chains of crystalline (4) are virtually identical to those we observed for crystalline (2) (Kolb *et al.*, 1996), but substantially different from the hydrogen-bonded three-dimensional packing structures of the related crystalline nucleosides (1) and (3) of urazole itself, with H atoms on N2 and N4 (Robinson *et al.*, 1996, 1997). Yet all four of these crystalline nucleosides were formed as single diastereomers, the specificity of each of which was related to the chirality of the sugar. These results suggest that this diastereospecificity may not be associated with the crystal packing of these nucleosides, but with their intrinsic molecular structure. Our work is currently focused on this problem.

Experimental

To a stirred solution of 4-methylurazole (Aldrich; 115 mg, 1 mmol) in 2.5 ml of water, 2-deoxy-D-ribose (Aldrich; 134 mg, 1 mmol) was added. The clear solution was kept in a stoppered flask at room temperature for six months; no crystallization was apparent. The flask was then unstoppered and left overnight, which led to the formation of a small mass of white crystals. The re-stoppered flask was set aside for three weeks, when no further crystallization was noticeable. The crystals were isolated by filtration, air dried and then dried *in vacuo* for 3 d [80 mg, m.p. 465 K (corr., brown spots), 470–471 K (corr., dec., bubbling brown liquid)] and used for the X-ray diffraction study. ¹H NMR (300 MHz; DMSO-*d*₆), δ : 1.57 (ddd, $J_{2'a,2'b} = 12.0$ Hz, $J_{2'a,3'} = 4.2$ Hz, $J_{2'a,1'} = 2.1$ Hz, 1H, H2'a), 2.02 (ddd, $J_{2'b,2'a} = J_{2'b,1'} = J_{2'b,3'} = 11.7$ Hz, 1H, H2'b), 2.89 (sharp s, 3H, N4-Me), 3.48 (*m*, 2H), 3.73 (*m*, 1H), 3.74 (*dd*, $J_{5'a,5'b} = 12$ Hz, $J = 1.8$ Hz, 1H), 4.51 (*d*, $J = 3.3$ Hz, 1H, OH), 4.88 (*br s*, 1H, OH), 5.02 (*dd*, $J_{1',2'b} = 11.4$ Hz, $J_{1',2'a} = 2.1$ Hz, 1H, H1'), 10.38 p.p.m. (*br s*, 1H, 2-NH). ¹³C NMR (75 MHz; DMSO-*d*₆), δ : 24.71 (N-Me), 31.57 (C-2'), 66.25 (C-5'), 67.58 (C-3'), 68.52 (C-4'), 81.05 (C-1'), 154.29 (C=O), 154.52 p.p.m. (C=O).

Crystal data

C₈H₁₃N₃O₅
M_r = 231.21
 Monoclinic
*P*2₁
a = 9.9110 (15) Å
b = 5.404 (2) Å
c = 10.0873 (13) Å
 β = 106.347 (10)^o
V = 518.4 (2) Å³
Z = 2
D_x = 1.481 Mg m⁻³
D_m not measured

Mo K α radiation

λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 11.49–18.78^o
 μ = 0.124 mm⁻¹
T = 296 K
 Blade
 0.43 × 0.31 × 0.11 mm
 Colorless

Data collection

Rigaku AFC-5S diffractometer
 ω scans (rate 4^o min⁻¹ in ω)

θ_{\max} = 30.05^o
h = 0 → 13
k = 0 → 7
l = -14 → 13

Absorption correction: none
 1839 measured reflections
 1666 independent reflections
 1150 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

Refinement on F^2
 $R(F) = 0.038$
 $wR(F^2) = 0.104$
 $S = 1.111$
 1666 reflections
 158 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$

3 standard reflections
 every 150 reflections
 intensity decay: 0.40%

$\Delta\rho_{\text{max}} = 0.241 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.224 \text{ e } \text{\AA}^{-3}$

Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)
 Absolute configuration:
 ascertained from the
 known configuration
 of the D-2-deoxyribose
 substrate
 Flack (1983) parameter =
 0.3 (17)

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

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2...O7 ⁱ	0.83 (3)	1.93 (3)	2.749 (3)	169 (3)
O8'—H8'...O7 ⁱⁱ	0.79 (5)	2.12 (5)	2.798 (4)	145 (6)
O7'—H7'...O8 ⁱⁱⁱ	0.70 (5)	2.00 (5)	2.693 (3)	168 (5)
C5'—H5'a...O6 ^{iv}	0.97	2.56	3.507 (4)	166

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

The H2, H7' and H8' atoms were refined isotropically. All other H atoms are riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *TEXSAN* and *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*, *SHELXL93* and *PLATON* (Spek, 1990).

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Quininium (S)-Mandelate†

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Abstract

The structure of the title compound, $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_2^+ \cdot \text{C}_8\text{H}_7\text{O}_3^-$, at 122 (1) K has been compared to those of the closely related cinchonidinium mandelate salts [Gjerløv & Larsen (1997). *Acta Cryst.* **B53**, 708–718]. The hydrogen-bonding arrangement of infinite chains of alternating anions and cations is identical to the hydrogen-bonding pattern seen in the diastereomeric mandelate salts of cinchonidine. Likewise, the herring-

† Alternative name: 6'-methoxycinchonidin-1-ium α -hydroxybenzeneacetate.