The base catalysed anomerisation of β -5-formyluridine; crystal and molecular structure of α -5-formyluridine

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ABSTRACT

On treatment with strong base β -5-formyluridine undergoes an anomerisation to give a mixture of the α - and β -anomers. The anomers have been separated by fractional recrystallisation and the absolute configuration of the α -anomer has been determined by X-ray analysis.

INTRODUCTION

In a recent communication¹ we described the synthesis of 5-formyluridine 5'-triphosphate, a potential affinity label for nucleoside triphosphate dependent enzymes. During the synthesis of the corresponding monophosphate by the method of Tener² a product was obtained which, on the basis of its nmr spectrum, we tentatively suggested was a mixture of the α - (1b) and β - (2b) anomers.

1 a) R = H
b) R = PO₃²⁻

2 a) R = H
b) R = PO₃²⁻

In order to confirm this unusual anomerisation we have studied the effects of the conditions of the Tener procedure on the nucleoside β -5-formyluridine (2a), and have isolated α -5-formyluridine (1a) after base treatment of 2a. The absolute configuration of the α -anomer has been established by X-ray analysis. The α -anomer of 5-formyluridine 5'-triphosphate has been used to affinity label³ E.coli DNA-dependent RNA-polymerase.

EXPERIMENTAL

General Procedure and Materials

Thin layer chromatography was carried out using 0.2 mm layer SiO₂ plates (PF-254) supplied by E. Merck and Co., Darmstadt (Germany). Paper chromatography was carried out by the descending method using Schleicher and Schüll 2043b (washed) paper in system A (ethanol - 1 M ammonium acetate, 7:3, v/v). The formyl derivatives were located by spraying with a saturated solution of σ -dianisidine in acetic acid.

Ultraviolet (UV) absorption spectra were recorded on a Cary model 16 spectrophotometer. Circular dichroism (CD) curves were obtained on a Cary 61 spectrophotometer. Nuclear magnetic resonance (NMR) ¹H-spectra were recorded on a Bruker-Physic HFX 60 spectrophotometer. Chemical shifts are given in δ units (parts per million) downfield from internal sodium 2,2,3,3-tetradeutero-3-(trimethylsilyl)propionate.

Melting points were recorded on a Kofler hot plate apparatus and are uncorrected.

β -5-Formyluridine (2a). 5-Formyluridine-2',3'-isopropylidene¹ (3 g) was dissolved in 50 % aqueous acetic acid (100 ml) and the solution was heated at 100°C for 90 minutes. The solvent was then removed in vacuo and the residue was evaporated from a further 20 ml of water. It was finally dissolved in hot methanol and left to crystallize at 4°C. After filtering, the crystals were washed with methanol and ether and dried. Yield 2.1 g (81 %), m. p. 197 - 198°C; $\lambda_{\text{max}}^{\text{H}_2\text{O}}$ 282 nm (ϵ 13.0 x 10³), 232 nm (ϵ 9.6 x 10³); N.M.R. 9.64 (1H,s), 8.85 (1H,s), 5.91 (1H,d,J = 2.5 Hz), 3.83 - 4.50 (5H,m). Anal. calcd. for C₁₀H₁₂N₂O₇: C 44.12; H 4.44; N 10.29. Found: C 44.14; H 4.46; N 10.20.

Base catalysed anomerisation of β -5-formyluridine (2a). 1 g of β -5-formyluridine was dissolved in 25 ml 4 N NaOH and 25 ml MeOH. After stirring for 30 minutes at room temperature the solution was then neutralised with Merck-I (H^+ -form) ion exchange resin. The resin was filtered off, washed well with water and the filtrate and washings were then evaporated in vacuo. A t.l.c. (Silica plate in acetone-benzene-water, 8:2:1, v/v) of the gummy residue indicated two major products, one of which ($R_f = 0.69$) gave a positive aldehyde test with o-dianisidine spray, and the other ($R_f = 0.41$) negative. The gummy residue was then dissolved in a little water and an excess of acetone was carefully added avoiding precipitation of the product. This solution was then applied to a Silica (10 g) column which was eluted with acetone-benzene (8:2, v/v). The aldehydic product eluted from the column in the first few fractions and after removal of the solvent an NMR spectrum indicated it to be a mixture of the α (1a) and β (2a) anomers of 5-formyluridine in the ratio of approx. 2:3. The mixture (0.68 g) was recrystallized from acetone-water yielding 209 mg of a material which was identical (NMR, UV, CD, m.p., mixed m.p.) to an authentic sample of β -5-formyluridine. The mother liquors were now enriched with the α -anomer and after removal of the solvent and repeated recrystallisation from MeOH-H₂O (3 - 4 times) 50 mg of pure α -5-formyluridine was obtained. m.p. 207-209°C. $\lambda_{max}^{H_2O}$ 282 nm (ϵ 13,400), 232 nm (ϵ 9,600). NMR 9.67 (1H,s), 8.52 (1H,s), 6.20 (1H,d,J = 4 Hz), 3.57 - 4.67 (5H,m). Anal. calcd. for C₁₀H₁₂N₂O₇: C 44.12; H 4.44; N 10.29. Found: C 44.17; H 4.44; N 10.26.

Further elution of the Silica column with acetone-benzene-water (8:2:1, v/v) yielded the non aldehydic product. Yield = 155 mg. Attempts to obtain this in a crystalline form and to characterise it have so far failed.

Crystal data

Small crystals of dimensions 0.06 x 0.10 x 0.16 mm were obtained by repeated crystallisation of α -5-formyluridine from MeOH-H₂O (3 - 4 times). Crystallographic data derived by photographic methods and from measurements using an automated STOE four circle diffractometer are presented in Table 1. Data were collected with Ni-filtered CuK α radiation in the θ -2 θ scan mode and corrected for geometrical factors but not absorption. Three check reflections monitored periodically after 100 reflections showed no significant loss of intensity.

TABLE 1: Crystallographic data.

Chemical formula	$C_{10}H_{12}N_2O_7$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Cell dimensions	$a = 5.932 \pm 0.002 \text{ \AA}$ $b = 6.174 \pm 0.002 \text{ \AA}$ $c = 29.588 \pm 0.006 \text{ \AA}$
Density calculated ($z = 4$)	$= 1.668 \text{ g}\cdot\text{cm}^{-3}$

Solution and Refinement of the Structure

According to Wilson's method⁴, an overall temperature ($B = 3.9 \text{ \AA}^2$) and scale factor were evaluated and used to compute normalised structure factors E 's⁵. The structure was solved by direct methods using MULTAN⁶ with a starting set consisting of five reflections. 32 different phase sets were obtained for the 125 normalised structure factors with $E > 1.5$, one of which was clearly more consistent than the others. The phase angles of this set were used to compute an E -map which revealed the whole structure, but atom O(5') was weakly indicated compared to other oxygen atoms. The structure was subjected to several cycles of isotropic and anisotropic full-matrix least squares refinement⁷ using a weighting scheme based on counter statistics⁸ and data with $F_{\text{obs}} \leq 3.0$. $\sigma_{F_{\text{obs}}}$ were treated as unobserved. A difference Fourier synthesis computed at this stage with atom O(5') omitted showed three peaks at relative weights 0.75 : 0.13 : 0.12 in locations which could be assigned to a disordered atom O(5'). This synthesis also provided all the hydrogen atom positions except the ones attached to O(5'), O(2'), O(3') atoms and displayed no other significant unaccounted peaks. The hydrogen atoms were included in the last two refinement cycles with the isotropic B 's of the atoms to which they are bound covalently and their parameters were held constant. In the last cycle the average parameter changes were less than one third of the standard deviations estimated from the correlation matrix. The final weighted R value is 5.2 %, the unweighted R is 8.6 % including unobserved reflections and 6.6 % omitting these.

RESULTS AND DISCUSSION

A The Anomerisation of β -5-formyluridine

β -5-Formyluridine was obtained in good yield from the acid hydrolysis of

5-formyl-2',3'-isopropylideneuridine. It has previously been prepared by the PtO_2 oxidation of 5-hydroxymethyluridine⁹. After treatment of β -5-formyluridine with 4 N NaOH/MeOH (1:1, v/v) for 30 min at room temperature two products could be detected by thin layer chromatography, one of which gave a positive and the other a negative aldehyde test with σ -dianisidine. These two products could be separated by chromatography over a Silica column, the crystalline aldehydic compound being the major component. An nmr spectrum of this compound was almost identical to that of 5-formyluridine 5'-monophosphate obtained from the β -cyanoethylphosphate procedure. Recrystallisation from acetone-water yielded starting material, β -5-formyluridine (confirmed by n.m.r., CD and mixed m.p.). The product in the mother liquors, which was now enriched in the other anomer, was recrystallised several times from methanol-water to yield pure α -5-formyluridine.

The signal for the C-1' proton in the nmr spectrum of the α -anomer is 0.29 ppm downfield from that of the corresponding proton of the β '-anomer. Such downfield shifts appear to be characteristic for anomeric pairs of ribose¹⁰ and 3'-deoxyribose¹¹ nucleosides. The CD spectra (Fig. 1) of the two anomers are virtually mirrorimages another common feature¹² of such anomeric pairs, although they differ in intensity. However, they do not follow the rule for pyrimidine nucleosides which states that β -D-nucleosides should have positive cotton effects in the 260 nm region while the α -D-nucleosides have negative cotton effects¹³. This is presumably due to the presence of the formyl group which has altered the electronic structure of the base chromophore as has been observed for uracil nucleosides containing $-\text{NH}_2$ and $-\text{N}_2^+$ groups at position 5¹².

This appears to be the first example of base catalysed anomerisation of a nucleoside with the exception of C-nucleosides such as pseudouridine^{14,15}. The anomerisation of pyrimidine nucleosides in an acidic medium has been reported¹⁶. Uridine and 5-bromouridine did not undergo any detectable anomerisation (by nmr) on treatment with 4 N NaOH/MeOH. It would therefore appear that the electron withdrawing formyl group influences this reaction. When the anomerisation was performed in the presence of D_2O none of the protons in the nmr-spectrum were exchanged. Any mechanism for this anomerisation would therefore appear to necessitate the opening of both the pyrimidine and ribose rings. One possibility is outlined in Scheme 1, and involves initial attack of hydroxide ion at the C-6 carbon of the activated double bond in the pyrimidine ring followed by opening of both the pyrimi-

Fig. 1

The circular dichroism curves of (a)----- α -5-formyluridine (b)——— β -5-formyluridine. The spectra were recorded in water at 20°C.

dine and ribose rings. Ring closure would then lead to formation of both the α - and β -anomers. It might be expected that pyranosyl isomers would also be formed, although these were not observed. Such isomers were detected in the acid catalysed anomerisation of pyrimidine nucleosides¹⁶ but recently other workers¹⁷ did not detect the presence of pyranosyl isomers after the base catalysed anomerisation of various C-glycosides.

SCHEME I

B X-ray structure of α -5-formyluridine. (Fig. 2)

In Tables 2 to 6 are presented final atomic coordinates, bond distances and angles, deviations of atoms from least squares planes through nucleobase and ribose, some relevant dihedral angles and a list of structure amplitudes. Figures 3, 4 and 5 describe the structure of the molecule and

Fig. 2

Chemical structure and numbering scheme for α -5-formyluridine.

Table 2.

Fractional atom coordinates and anisotropic temperature factors with standard deviations

Atomic coordinates of α -5-formyluridine in fractions of the crystallographic axes and

thermal parameters in the form:
 $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	X	Y	Z	$B(11)$	$B(22)$	$B(33)$	$B(12)$	$B(13)$	$B(23)$
A(1)	0.0198(10)	0.5788(9)	0.1598(2)	187(18)	212(16)	7(1)	1(17)	6(3)	-2(4)
C(2)	0.0414(13)	0.6931(12)	0.1930(2)	245(29)	235(25)	14(1)	35(24)	15(3)	-16(3)
N(3)	0.0638(18)	0.8544(19)	0.2170(2)	370(40)	198(16)	8(1)	-24(17)	11(3)	-11(3)
C(4)	0.3745(13)	0.6357(17)	0.2096(2)	270(20)	187(20)	8(1)	43(23)	-5(4)	10(4)
O(4)	0.5500(18)	0.4574(18)	0.3144(2)	253(18)	220(14)	12(1)	-5(16)	21(3)	22(3)
C(5)	0.2917(12)	0.4441(11)	0.1756(2)	208(24)	181(19)	8(1)	32(20)	3(4)	2(3)
C(6)	0.1027(11)	0.3566(11)	0.1518(2)	223(17)	231(21)	11(1)	-27(22)	-9(4)	-10(4)
C(7)	0.4199(11)	0.1237(11)	0.1649(2)	223(16)	223(16)	14(1)	-15(14)	1(3)	10(4)
C(1)	0.2166(12)	0.6018(11)	0.1311(2)	224(25)	230(22)	10(1)	15(22)	9(4)	-2(4)
C(2')	0.1584(17)	0.7692(12)	0.0849(2)	310(35)	354(42)	11(1)	46(21)	-14(3)	-2(4)
O(3')	0.0778(13)	0.7548(18)	0.0561(2)	210(25)	324(18)	8(1)	-15(22)	-6(4)	-1(3)
C(3')	0.2393(19)	0.6866(18)	0.0170(2)	310(37)	354(42)	11(1)	17(22)	-10(3)	-1(3)
C(4')	0.2932(19)	0.4448(12)	0.0610(2)	210(24)	324(18)	8(1)	-15(22)	1(4)	-3(4)
C(5')	0.4850(16)	0.4106(17)	0.0795(2)	238(21)	245(18)	8(1)	15(21)	1(4)	-1(3)
C(5')	0.5942(17)	0.3140(12)	0.0393(2)	237(17)	247(14)	12(1)	60(28)	10(5)	-10(5)
O(5')	0.4734(14)	0.3573(12)	0.0452(2)	237(12)	237(12)	12(1)	56(26)	15(5)	-17(5)
O(5'A)	0.4830(16)	0.3768(12)	0.0452(2)	237(12)	237(12)	12(1)	56(26)	15(5)	-17(5)
H(1E)	0.2860(10)	0.7521(10)	0.1265(1)	170(1)	145(1)	7(1)	0(0)	4(0)	3(0)
H(1F)	0.3469(10)	0.6663(10)	0.1497(1)	170(1)	145(1)	8(1)	0(0)	4(0)	3(0)
H(1G)	0.3978(10)	0.5653(10)	0.1091(1)	170(1)	145(1)	8(1)	0(0)	4(0)	3(0)
H(3')	0.4738(10)	0.7321(10)	0.0594(1)	170(1)	145(1)	9(1)	0(0)	4(0)	3(0)
H(3'A)	0.4867(10)	0.7347(10)	0.0464(1)	170(1)	145(1)	11(1)	0(0)	4(0)	3(0)
H(5'B)	0.4570(10)	0.3420(10)	0.0064(1)	170(1)	145(1)	11(1)	0(0)	4(0)	3(0)
H(5'C)	0.6333(10)	0.3649(10)	0.0523(1)	170(1)	145(1)	11(1)	0(0)	4(0)	3(0)

Table 3 Bond distances and angles.

Averaged standard deviations in bond lengths is 0.008 Å and in bond angles is 0.6°. Positions of hydrogen atoms given in Table 2 were found from difference Fouriers, C-H distance is between 0.73 Å and 1.06 Å, C-C-H and C-O-H angles are at 90° to 115°.

Bond length in Å		Bond angle in °	
N(1)-C(2)	1.392	C(2)-N(1)-C(6)	122.4
N(1)-C(6)	1.357	C(2)-N(1)-C(1')	115.4
N(1)-C(1')	1.501	C(6)-N(1)-C(1')	122.1
C(2)-O(2)	1.217	N(1)-C(2)-O(2)	122.6
C(2)-N(3)	1.399	N(1)-C(2)-N(3)	114.7
N(3)-C(4)	1.387	O(2)-C(2)-N(3)	122.7
C(4)-O(4)	1.232	C(2)-N(3)-C(4)	126.2
C(4)-C(5)	1.451	N(3)-C(4)-O(4)	117.9
C(5)-C(6)	1.358	N(3)-C(4)-C(5)	114.7
C(5)-C(7)	1.463	O(4)-C(4)-C(5)	127.5
C(7)-O(7)	1.231	C(4)-C(5)-C(6)	119.8
C(1')-C(2')	1.523	C(4)-C(5)-C(7)	120.2
C(1')-O(4')	1.416	C(6)-C(5)-C(7)	120.0
C(2')-O(2')	1.431	N(1)-C(6)-C(5)	122.2
C(2')-C(3')	1.536	C(5)-C(7)-O(7)	124.6
C(3')-O(3')	1.409	N(1)-C(1')-C(2')	113.3
C(3')-C(4')	1.503	N(1)-C(1')-O(4')	106.8
C(4')-O(4')	1.453	C(2')-C(1')-O(4')	108.5
C(4')-C(5')	1.534	C(1')-C(2')-O(2')	112.2
C(5')-O(5')	1.364	C(1')-C(2')-C(3')	100.0
C(5')-O(5'A)	1.272	O(2')-C(2')-C(3')	108.7
C(5')-O(5'B)	1.395	C(2')-C(3')-O(3')	112.8
		C(2')-C(3')-C(4')	102.6
		O(3')-C(3')-C(4')	114.0
		C(3')-C(4')-O(4')	103.9
		C(3')-C(4')-C(5')	115.9
		O(4')-C(4')-C(5')	109.2
		C(1')-O(4')-C(4')	108.9
		C(4')-C(5')-O(5')	115.5
		C(4')-C(5')-O(5'A)	114.8
		C(4')-C(5')-O(5'B)	104.1
		O(5')-C(5')-O(5'A)	100.0
		O(5')-C(5')-O(5'B)	108.5
		O(5'A)-C(5')-O(5'B)	114.3

Table 4 Least squares planes through heterocycle and sugar.

The equations of the planes are of the form $lx + my + nz + p = 0$

where x, y, z are along a, b, c . Atoms which define the planes are marked by +.

1. <u>Heterocycles</u>			
$l = 0.5414$	$m = -0.4975$	$n = 0.6778$	$p = -1.6214$
Atoms	Displacement ($\text{\AA}$)		
N(1)+	-0.010		
N(3)+	0.018		
C(2)+	-0.002		
C(4)+	-0.026		
C(5)+	0.019		
C(6)+	-0.002		
O(2)	-0.041		
O(4)	-0.112		
C(7)	-0.009		
O(7)	0.026		
C(1')	-0.145		
H(7)	-0.067		
2. <u>Sugar</u>			
$l = 0.9367$	$m = 0.3477$	$n = 0.0414$	$p = -2.6497$
Atoms	Displacement ($\text{\AA}$)		
C(1')+	0.007		
C(2')+	-0.004		
C(3')+	0.604		
C(4')+	-0.004		
O(4')+	-0.007		
N(1)	-1.193		
O(2')	-1.332		
O(3')	0.332		
C(5')	0.769		

Table 5 Some dihedral angles describing the conformation of α -5-formyluridine molecule.

These four-atom angles A-B-C-D are defined as zero if, when looking from B to C, bonds A-B and C-D are cis-planar. The angle is counted positive if the far bond C-D is rotated clockwise with respect to the near bond A-B.

A-B-C-D	Angle in degrees
C(6)-N(1)-C(1')-O(4')	-21.6
C(1')-C(2')-C(3')-C(4')	37.6
C(2')-C(3')-C(4')-O(4')	-38.3
C(3')-C(4')-O(4')-C(1')	23.4
C(4')-O(4')-C(1')-C(2')	1.3
O(4')-C(1')-C(2')-C(3')	-24.5
O(4')-C(4')-C(5')-O(5')	-55.1
O(4')-C(4')-C(5')-O(5'A)	60.3
O(4')-C(4')-C(5')-O(5'B)	-174.0
O(3')-C(3')-C(4')-O(4')	-160.6
O(2')-C(2')-C(3')-C(4')	-80.1
O(7)-C(7)-C(5)-C(4)	180.0
O(5')-C(5')-C(4')-C(3')	61.7
O(5'A)-C(5')-C(4')-C(3')	177.1
O(5'B)-C(5')-C(4')-C(3')	-57.2

Table 6.

Alpha-formyluridine FO FC table

Observed and calculated structure factors for α -5-formyluridine multiplied by 10.

H	K	L	F OBS	F CAL	H	K	L	F OBS	F CAL	H	K	L	F OBS	F CAL
0	0	4	318	321	0	2	11	146	141	0	4	8	97	100
0	0	6	199	208	0	2	12	263	262	0	4	9	61	55
0	0	8	444	471	0	2	13	36	31	0	4	10	35	28
0	0	10	63	91	0	2	14	119	111	0	4	11	90	95
0	0	12	163	171	0	2	15	108	97	0	4	12	194	197
0	0	14	360	367	0	2	16	64	43	0	4	13	200	206
0	0	16	39	28	0	2	17	2	14	0	4	14	54	36
0	0	18	245	244	0	2	18	165	167	0	4	15	75	75
0	0	20	150	154	0	2	19	90	84	0	4	16	2	0
0	0	22	26	18	0	2	20	2	30	0	4	17	2	27
0	0	24	46	23	0	2	21	144	150	0	4	18	122	120
0	0	26	72	77	0	2	22	88	86	0	4	19	54	45
0	0	28	118	124	0	2	23	51	58	0	4	20	71	60
0	0	30	15	14	0	2	24	47	19	0	4	21	86	76
0	0	32	19	19	0	2	25	150	150	0	4	22	68	62
0	0	34	29	41	0	2	26	2	14	0	4	23	96	100
0	1	1	334	343	0	2	27	35	24	0	4	24	34	20
0	1	2	699	771	0	2	28	48	34	0	4	25	89	85
0	1	3	29	0	0	2	29	49	80	0	4	26	37	50
0	1	4	20	20	0	2	30	84	106	0	4	27	23	32
0	1	5	62	62	0	2	31	49	61	0	4	28	33	34
0	1	6	490	497	0	2	32	2	26	0	5	1	157	145
0	1	7	415	438	0	3	1	537	546	0	5	2	54	40
0	1	8	260	276	0	3	2	255	263	0	5	3	54	50
0	1	9	547	552	0	3	3	236	233	0	5	4	107	103
0	1	10	201	205	0	3	4	115	115	0	5	5	159	176
0	1	11	368	369	0	3	5	106	116	0	5	6	209	212
0	1	12	383	397	0	3	6	77	84	0	5	7	279	299
0	1	13	148	147	0	3	7	360	358	0	5	8	125	144
0	1	14	46	50	0	3	8	227	227	0	5	9	193	198
0	1	15	450	440	0	3	9	159	161	0	5	10	202	218
0	1	16	347	352	0	3	10	54	58	0	5	11	105	118
0	1	17	342	334	0	3	11	196	190	0	5	12	38	23
0	1	18	71	47	0	3	12	148	153	0	5	13	131	134
0	1	19	152	145	0	3	13	154	153	0	5	14	3	10
0	1	20	279	261	0	3	14	231	230	0	5	15	85	94
0	1	21	36	63	0	3	15	110	114	0	5	16	105	87
0	1	22	26	49	0	3	16	42	40	0	5	17	70	72
0	1	23	27	6	0	3	17	119	117	0	5	18	28	18
0	1	24	35	53	0	3	18	37	20	0	5	19	27	26
0	1	25	24	26	0	3	19	104	114	0	5	20	2	2
0	1	26	31	59	0	3	20	120	117	0	5	21	52	36
0	1	27	125	138	0	3	21	2	18	0	5	22	2	2
0	1	28	38	21	0	3	22	31	2	0	5	23	21	25
0	1	29	112	135	0	3	23	139	147	0	5	24	21	31
0	1	30	20	42	0	3	24	128	117	0	6	0	2	12
0	1	31	41	40	0	3	25	26	1	0	6	1	98	106
0	1	32	18	47	0	3	26	105	122	0	6	2	65	71
0	1	33	38	46	0	3	27	2	17	0	6	3	43	24
0	2	0	268	271	0	3	28	60	50	0	6	4	50	45
0	2	1	302	312	0	3	29	40	38	0	6	5	63	62
0	2	2	613	649	0	3	30	35	3	0	6	6	103	102
0	2	3	268	274	0	4	0	78	80	0	6	7	32	48
0	2	4	283	292	0	4	1	98	101	0	6	8	100	100
0	2	5	281	298	0	4	2	173	173	0	6	9	38	30
0	2	6	53	62	0	4	3	81	84	0	6	10	52	63
0	2	7	70	65	0	4	4	34	9	0	6	11	41	34
0	2	8	419	430	0	4	5	206	210	0	6	12	75	76
0	2	9	71	79	0	4	6	99	102	0	6	13	28	26
0	2	10	383	379	0	4	7	215	220	0	6	14	29	26

ALPHA-FORMYLURIDINE					FO	FC	TABLE									
H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL		
0	6	15	52	50	1	1	18	64	64	1	3	11	135	151		
0	6	16	2	21	1	1	19	64	66	1	3	12	105	105		
0	6	17	2	17	1	1	20	114	119	1	3	13	137	141		
0	6	18	28	27	1	1	21	146	143	1	3	14	68	78		
0	7	1	20	11	1	1	22	67	68	1	3	15	36	58		
0	7	2	33	40	1	1	23	149	144	1	3	16	187	179		
0	7	3	30	38	1	1	24	111	108	1	3	17	92	85		
0	7	4	30	32	1	1	25	183	176	1	3	18	55	21		
0	7	5	2	14	1	1	26	97	92	1	3	19	143	157		
1	0	1	58	59	1	1	27	2	19	1	3	20	137	140		
1	0	2	81	96	1	1	28	56	39	1	3	21	99	112		
1	0	3	97	90	1	1	29	89	95	1	3	22	19	39		
1	0	4	883	917	1	1	30	91	92	1	3	23	153	166		
1	0	5	551	558	1	1	31	40	62	1	3	24	66	70		
1	0	6	221	235	1	1	32	65	72	1	3	25	2	35		
1	0	7	2	20	1	1	33	35	26	1	3	26	26	39		
1	0	8	75	99	1	2	0	155	147	1	3	27	61	68		
1	0	9	633	652	1	2	1	485	470	1	3	28	59	52		
1	0	10	290	289	1	2	2	60	69	1	3	29	56	56		
1	0	11	30	41	1	2	3	44	42	1	3	30	39	38		
1	0	12	374	390	1	2	4	213	197	1	4	0	246	239		
1	0	13	230	224	1	2	5	155	151	1	4	1	137	126		
1	0	14	62	69	1	2	6	157	139	1	4	2	177	164		
1	0	15	321	319	1	2	7	459	445	1	4	3	203	183		
1	0	16	129	131	1	2	8	227	235	1	4	4	42	45		
1	0	17	270	252	1	2	9	521	517	1	4	5	129	123		
1	0	18	170	149	1	2	10	260	266	1	4	6	214	216		
1	0	19	236	226	1	2	11	222	216	1	4	7	94	87		
1	0	20	121	129	1	2	12	117	112	1	4	8	105	113		
1	0	21	164	148	1	2	13	110	103	1	4	9	183	187		
1	0	22	308	309	1	2	14	42	46	1	4	10	75	63		
1	0	23	111	103	1	2	15	230	237	1	4	11	124	118		
1	0	24	2	11	1	2	16	256	246	1	4	12	38	37		
1	0	25	66	60	1	2	17	203	199	1	4	13	169	164		
1	0	26	58	52	1	2	18	107	93	1	4	14	220	217		
1	0	27	156	162	1	2	19	125	126	1	4	15	86	84		
1	0	28	2	39	1	2	20	84	84	1	4	16	91	82		
1	0	29	31	22	1	2	21	138	126	1	4	17	250	244		
1	0	30	75	63	1	2	22	129	116	1	4	18	86	77		
1	0	31	51	90	1	2	23	94	101	1	4	19	95	93		
1	0	32	54	76	1	2	24	119	115	1	4	20	114	112		
1	0	33	55	75	1	2	25	2	20	1	4	21	48	31		
1	1	0	326	341	1	2	26	84	84	1	4	22	77	74		
1	1	1	248	240	1	2	27	69	81	1	4	23	75	80		
1	1	2	786	803	1	2	28	39	35	1	4	24	59	52		
1	1	3	560	564	1	2	29	17	8	1	4	25	51	53		
1	1	4	601	575	1	2	30	17	24	1	4	26	33	22		
1	1	5	235	249	1	2	31	20	23	1	4	27	32	35		
1	1	6	595	591	1	2	32	2	14	1	5	0	125	116		
1	1	7	893	886	1	3	0	435	414	1	5	1	74	68		
1	1	8	496	499	1	3	1	237	233	1	5	2	92	85		
1	1	9	535	524	1	3	2	192	166	1	5	3	130	134		
1	1	10	330	338	1	3	3	170	152	1	5	4	78	86		
1	1	11	115	97	1	3	4	293	285	1	5	5	46	24		
1	1	12	236	231	1	3	5	186	163	1	5	6	47	48		
1	1	13	202	185	1	3	6	170	155	1	5	7	27	36		
1	1	14	59	67	1	3	7	102	95	1	5	8	60	62		
1	1	15	2	37	1	3	8	58	66	1	5	9	92	83		
1	1	16	208	210	1	3	9	108	97	1	5	10	94	97		
1	1	17	183	174	1	3	10	135	133	1	5	11	155	157		

Table 6 (continued)

ALPHA-FORMYLURIDINE					FO FC TABLE									
H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
1	5	12	107	114	2	0	27	206	191	2	2	21	160	157
1	5	13	66	76	2	0	28	94	104	2	2	22	40	37
1	5	14	191	194	2	0	29	122	135	2	2	23	51	67
1	5	15	122	121	2	0	30	81	86	2	2	24	98	85
1	5	16	39	30	2	0	31	23	21	2	2	25	74	70
1	5	17	22	30	2	0	32	11	3	2	2	26	70	72
1	5	18	37	27	2	1	0	12	11	2	2	27	2	10
1	5	19	28	40	2	1	1	444	442	2	2	28	81	80
1	5	20	55	60	2	1	2	324	312	2	2	29	20	9
1	5	21	30	36	2	1	3	426	422	2	2	30	17	27
1	5	22	2	19	2	1	4	233	224	2	2	31	21	30
1	5	23	53	59	2	1	5	294	300	2	3	0	235	231
1	6	0	198	201	2	1	6	127	118	2	3	1	202	193
1	6	1	36	54	2	1	7	352	346	2	3	2	250	241
1	6	2	182	175	2	1	8	428	424	2	3	3	243	221
1	6	3	136	132	2	1	9	316	330	2	3	4	237	224
1	6	4	2	5	2	1	10	120	125	2	3	5	82	82
1	6	5	80	84	2	1	11	344	331	2	3	6	111	106
1	6	6	108	110	2	1	12	141	139	2	3	7	183	164
1	6	7	52	44	2	1	13	173	175	2	3	8	68	62
1	6	8	50	45	2	1	14	349	349	2	3	9	164	166
1	6	9	2	21	2	1	15	105	100	2	3	10	80	71
1	6	10	51	79	2	1	16	121	109	2	3	11	127	123
1	6	11	14	15	2	1	17	2	19	2	3	12	147	144
1	6	12	13	25	2	1	18	76	66	2	3	13	118	125
1	6	13	2	16	2	1	19	66	60	2	3	14	66	58
1	6	14	2	13	2	1	20	176	176	2	3	15	77	90
1	6	15	17	7	2	1	21	2	26	2	3	16	126	124
1	6	16	28	36	2	1	22	16	30	2	3	17	95	95
1	6	17	18	22	2	1	23	158	153	2	3	18	2	37
1	7	0	56	56	2	1	24	131	135	2	3	19	206	200
1	7	1	33	35	2	1	25	132	132	2	3	20	116	104
1	7	2	9	16	2	1	26	73	71	2	3	21	138	133
2	0	0	171	167	2	1	27	61	65	2	3	22	28	53
2	0	1	14	31	2	1	28	64	60	2	3	23	169	163
2	0	2	512	503	2	1	29	41	50	2	3	24	95	86
2	0	3	414	398	2	1	30	41	47	2	3	25	2	32
2	0	4	151	138	2	1	31	2	14	2	3	26	76	78
2	0	5	238	242	2	1	32	26	39	2	3	27	55	45
2	0	6	242	241	2	2	0	126	126	2	3	28	48	43
2	0	7	254	251	2	2	1	180	174	2	3	29	32	25
2	0	8	293	291	2	2	2	135	110	2	4	0	58	63
2	0	9	22	40	2	2	3	394	384	2	4	1	2	22
2	0	10	151	142	2	2	4	237	233	2	4	2	140	124
2	0	11	40	33	2	2	5	178	169	2	4	3	209	202
2	0	12	219	212	2	2	6	454	426	2	4	4	114	113
2	0	13	175	175	2	2	7	160	148	2	4	5	47	44
2	0	14	73	79	2	2	8	200	202	2	4	6	204	187
2	0	15	120	123	2	2	9	155	144	2	4	7	136	139
2	0	16	210	213	2	2	10	91	85	2	4	8	62	60
2	0	17	160	140	2	2	11	188	183	2	4	9	104	95
2	0	18	284	275	2	2	12	262	267	2	4	10	67	77
2	0	19	48	45	2	2	13	291	277	2	4	11	84	76
2	0	20	72	72	2	2	14	246	237	2	4	12	59	64
2	0	21	27	38	2	2	15	266	257	2	4	13	86	89
2	0	22	31	21	2	2	16	156	156	2	4	14	33	40
2	0	23	155	153	2	2	17	162	158	2	4	15	27	26
2	0	24	138	144	2	2	18	169	163	2	4	16	121	128
2	0	25	46	32	2	2	19	110	108	2	4	17	143	144
2	0	26	351	345	2	2	20	59	57	2	4	18	84	90

ALPHA-FORMYLURIDINE					FO FC TABLE									
H	K	L	FQBS	FCAL	H	K	L	FQBS	FCAL	H	K	L	FQBS	FCAL
2	4	19	65	45	3	0	14	34	28	3	2	12	130	113
2	4	20	68	68	3	0	15	129	128	3	2	13	78	79
2	4	21	126	124	3	0	16	236	226	3	2	14	210	211
2	4	22	50	46	3	0	17	60	70	3	2	15	136	133
2	4	23	73	69	3	0	18	81	68	3	2	16	123	122
2	4	24	23	18	3	0	19	100	96	3	2	17	140	131
2	4	25	57	73	3	0	20	96	73	3	2	18	112	100
2	4	26	20	13	3	0	21	204	208	3	2	19	136	147
2	5	0	56	56	3	0	22	90	87	3	2	20	72	68
2	5	1	54	45	3	0	23	26	31	3	2	21	92	85
2	5	2	137	134	3	0	24	26	5	3	2	22	50	55
2	5	3	61	65	3	0	25	5	17	3	2	23	41	42
2	5	4	40	28	3	0	26	58	59	3	2	24	44	33
2	5	5	70	71	3	0	27	45	29	3	2	25	62	68
2	5	6	60	51	3	0	28	2	26	3	2	26	92	101
2	5	7	12	23	3	0	29	11	8	3	2	27	85	100
2	5	8	62	50	3	0	30	2	8	3	2	28	109	120
2	5	9	95	102	3	1	0	2	8	3	2	29	7	14
2	5	10	111	111	3	1	1	157	142	3	3	0	89	86
2	5	11	35	50	3	1	2	121	126	3	3	1	183	178
2	5	12	58	57	3	1	3	264	267	3	3	2	103	91
2	5	13	84	91	3	1	4	157	148	3	3	3	138	136
2	5	14	57	67	3	1	5	238	229	3	3	4	173	165
2	5	15	13	30	3	1	6	193	179	3	3	5	74	79
2	5	16	14	41	3	1	7	189	180	3	3	6	65	58
2	5	17	82	80	3	1	8	189	173	3	3	7	144	140
2	5	18	80	74	3	1	9	192	196	3	3	8	98	93
2	5	19	100	104	3	1	10	170	164	3	3	9	164	160
2	5	20	26	28	3	1	11	167	165	3	3	10	27	41
2	5	21	78	88	3	1	12	188	189	3	3	11	22	20
2	5	22	57	68	3	1	13	133	129	3	3	12	48	54
2	6	0	41	40	3	1	14	50	74	3	3	13	105	101
2	6	1	75	87	3	1	15	66	63	3	3	14	191	193
2	6	2	92	91	3	1	16	146	133	3	3	15	89	103
2	6	3	38	20	3	1	17	252	239	3	3	16	29	48
2	6	4	59	66	3	1	18	96	90	3	3	17	95	104
2	6	5	75	82	3	1	19	250	241	3	3	18	120	118
2	6	6	49	55	3	1	20	175	167	3	3	19	84	92
2	6	7	63	72	3	1	21	181	180	3	3	20	137	137
2	6	8	55	61	3	1	22	88	93	3	3	21	155	150
2	6	9	45	54	3	1	23	127	130	3	3	22	23	20
2	6	10	49	51	3	1	24	116	115	3	3	23	54	65
2	6	11	2	27	3	1	25	41	50	3	3	24	53	52
2	6	12	39	34	3	1	26	39	29	3	3	25	75	82
2	6	13	39	21	3	1	27	48	63	3	3	26	81	95
2	6	14	32	29	3	1	28	59	65	3	4	0	126	123
2	6	15	39	49	3	1	29	37	22	3	4	1	113	110
3	0	1	348	342	3	1	30	5	17	3	4	2	101	98
3	0	2	421	408	3	2	0	108	107	3	4	3	62	64
3	0	3	167	174	3	2	1	117	105	3	4	4	73	70
3	0	4	342	334	3	2	2	22	20	3	4	5	104	105
3	0	5	215	206	3	2	3	217	215	3	4	6	197	193
3	0	6	414	395	3	2	4	158	163	3	4	7	101	87
3	0	7	275	253	3	2	5	197	206	3	4	8	135	137
3	0	8	226	212	3	2	6	105	101	3	4	9	120	120
3	0	9	185	169	3	2	7	58	57	3	4	10	58	45
3	0	10	86	75	3	2	8	46	34	3	4	11	88	88
3	0	11	135	113	3	2	9	152	146	3	4	12	152	160
3	0	12	32	43	3	2	10	112	99	3	4	13	145	152
3	0	13	210	215	3	2	11	75	82	3	4	14	50	48

Table 6 (continued)

ALPHA-FORMYLURIDINE					FO	FC	TABLE					H	K	L	FOBS	FCAL
H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL		
3	4	15	92	87	4	0	21	101	107	4	2	25	23	36		
3	4	16	151	149	4	0	22	30	20	4	3	0	48	52		
3	4	17	2	21	4	0	23	105	103	4	3	1	143	141		
3	4	18	48	41	4	0	24	6	30	4	3	2	28	52		
3	4	19	54	67	4	0	25	6	5	4	3	3	155	148		
3	4	20	75	75	4	0	26	2	22	4	3	4	126	118		
3	4	21	54	54	4	0	27	26	21	4	3	5	126	124		
3	4	22	2	26	4	1	0	33	1	4	3	6	177	180		
3	4	23	47	51	4	1	1	113	113	4	3	7	174	167		
3	5	0	41	55	4	1	2	256	257	4	3	8	138	146		
3	5	1	36	105	4	1	3	202	205	4	3	9	60	59		
3	5	2	58	53	4	1	4	180	177	4	3	10	72	68		
3	5	3	76	81	4	1	5	197	196	4	3	11	15	7		
3	5	4	89	89	4	1	6	160	142	4	3	12	122	115		
3	5	5	69	74	4	1	7	121	125	4	3	13	22	27		
3	5	6	39	41	4	1	8	128	129	4	3	14	102	87		
3	5	7	44	47	4	1	9	40	43	4	3	15	42	58		
3	5	8	89	88	4	1	10	173	168	4	3	16	89	93		
3	5	9	30	39	4	1	11	25	42	4	3	17	101	106		
3	5	10	2	5	4	1	12	170	164	4	3	18	91	99		
3	5	11	33	41	4	1	13	57	78	4	3	19	45	51		
3	5	12	85	85	4	1	14	28	6	4	3	20	2	16		
3	5	13	20	25	4	1	15	89	98	4	3	21	57	48		
3	5	14	60	64	4	1	16	61	61	4	3	22	74	83		
3	5	15	107	116	4	1	17	52	54	4	3	23	69	86		
3	5	16	37	45	4	1	18	112	117	4	4	0	69	74		
3	5	17	2	14	4	1	19	47	53	4	4	1	75	72		
3	5	18	47	55	4	1	20	36	46	4	4	2	88	85		
3	6	0	48	48	4	1	21	103	95	4	4	3	65	67		
3	6	1	46	50	4	1	22	25	11	4	4	4	172	165		
3	6	2	56	55	4	1	23	26	45	4	4	5	44	50		
3	6	3	22	1	4	1	24	30	33	4	4	6	111	118		
3	6	4	2	18	4	1	25	18	5	4	4	7	110	102		
3	6	5	2	7	4	1	26	36	25	4	4	8	47	48		
3	6	6	30	28	4	1	27	28	55	4	4	9	87	83		
3	6	7	35	30	4	2	0	84	80	4	4	10	93	94		
3	6	8	32	30	4	2	1	238	222	4	4	11	84	90		
3	6	9	15	31	4	2	2	46	33	4	4	12	100	104		
3	6	10	10	13	4	2	3	73	76	4	4	13	22	10		
4	0	0	221	221	4	2	4	114	108	4	4	14	68	61		
4	0	1	138	145	4	2	5	134	132	4	4	15	34	48		
4	0	2	89	82	4	2	6	157	136	4	4	16	57	54		
4	0	3	38	21	4	2	7	2	42	4	4	17	13	34		
4	0	4	207	220	4	2	8	135	132	4	4	18	43	28		
4	0	5	2	51	4	2	9	94	91	4	4	19	27	16		
4	0	6	34	60	4	2	10	80	80	4	5	0	122	122		
4	0	7	30	24	4	2	11	201	196	4	5	1	24	12		
4	0	8	2	24	4	2	12	238	229	4	5	2	67	77		
4	0	9	63	50	4	2	13	136	145	4	5	3	48	54		
4	0	10	13	5	4	2	14	192	193	4	5	4	36	45		
4	0	11	2	4	4	2	15	134	138	4	5	5	50	61		
4	0	12	31	6	4	2	16	133	140	4	5	6	49	50		
4	0	13	123	124	4	2	17	2	35	4	5	7	2	14		
4	0	14	81	92	4	2	18	59	39	4	5	8	77	73		
4	0	15	2	28	4	2	19	42	47	4	5	9	23	40		
4	0	16	98	97	4	2	20	41	45	4	5	10	42	42		
4	0	17	57	65	4	2	21	21	40	4	5	11	63	67		
4	0	18	125	126	4	2	22	57	45	4	5	12	2	22		
4	0	19	247	259	4	2	23	24	8	4	5	13	45	45		
4	0	20	56	52	4	2	24	45	64	5	0	1	2	38		

ALPHA-FORMYLURIDINE					FO	FC	TABLE					H	K	L	FOBS	FCAL
H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL		
5	C	2	49	38	5	2	15	28	46	6	1	4	22	23		
5	C	3	186	199	5	2	16	2	16	6	1	5	107	143		
5	C	4	72	80	5	2	17	39	42	6	1	6	16	28		
5	C	5	195	200	5	2	18	50	58	6	1	7	45	62		
5	C	6	2	8	5	2	19	27	35	6	1	8	86	112		
5	C	7	63	49	5	2	20	45	59	6	1	9	67	95		
5	C	8	94	110	5	2	21	40	43	6	1	10	39	63		
5	C	9	64	35	5	3	0	82	75	6	1	11	47	61		
5	C	10	182	189	5	3	1	93	98	6	1	12	32	55		
5	C	11	93	83	5	3	2	158	158	6	1	13	19	18		
5	C	12	60	68	5	3	3	115	109	6	1	14	22	13		
5	C	13	2	25	5	3	4	126	143	6	1	15	43	68		
5	C	14	2	37	5	3	5	75	82	6	2	0	48	48		
5	C	15	133	142	5	3	6	65	64	6	2	1	2	14		
5	C	16	8	16	5	3	7	16	22	6	2	2	2	13		
5	C	17	26	17	5	3	8	79	91	6	2	3	38	34		
5	C	18	4	28	5	3	9	128	137	6	2	4	2	44		
5	C	19	2	10	5	3	10	66	66	6	2	5	33	25		
5	C	20	2	2	5	3	11	44	48	6	2	6	68	89		
5	C	21	57	71	5	3	12	73	74	6	2	7	23	7		
5	C	22	2	67	5	3	13	28	43	6	2	8	28	30		
5	C	23	16	45	5	3	14	31	36	6	2	9	29	44		
5	1	0	35	30	5	3	15	71	73	6	2	10	53	68		
5	1	1	139	139	5	3	16	14	9	6	2	11	34	40		
5	1	2	108	93	5	3	17	36	33	6	2	12	32	41		
5	1	3	71	77	5	3	18	35	24	6	2	13	10	15		
5	1	4	44	37	5	4	0	2	15	6	3	0	91	130		
5	1	5	155	152	5	4	1	9	24	6	3	1	26	37		
5	1	6	43	52	5	4	2	49	60	6	3	2	2	28		
5	1	7	78	81	5	4	3	2	18	6	3	3	2	22		
5	1	8	73	97	5	4	4	88	82	6	3	4	45	46		
5	1	9	143	139	5	4	5	32	45	6	3	5	14	28		
5	1	10	75	71	5	4	6	53	58	6	3	6	39	65		
5	1	11	6	15	5	4	7	23	28	6	3	7	33	40		
5	1	12	46	80	5	4	8	59	68							
5	1	13	28	24	5	4	9	45	46							
5	1	14	17	31	5	4	10	42	69							
5	1	15	30	23	5	4	11	30	26							
5	1	16	72	79	5	4	12	50	50							
5	1	17	99	104	6	0	0	56	59							
5	1	18	70	77	6	0	1	64	62							
5	1	19	66	61	6	0	2	56	77							
5	1	20	25	17	6	0	3	31	36							
5	1	21	44	57	6	0	4	41	37							
5	1	22	27	27	6	0	5	2	47							
5	2	0	241	259	6	0	6	2	26							
5	2	1	139	136	6	0	7	116	141							
5	2	2	174	178	6	0	8	2	2							
5	2	3	88	38	6	0	9	63	88							
5	2	4	111	101	6	0	10	46	76							
5	2	5	139	145	6	0	11	24	74							
5	2	6	70	72	6	0	12	44	35							
5	2	7	133	129	6	0	13	2	9							
5	2	8	100	97	6	0	14	56	83							
5	2	9	53	52	6	0	15	31	21							
5	2	10	65	68	6	0	16	22	35							
5	2	11	69	75	6	1	0	43	40							
5	2	12	63	69	6	1	1	41	46							
5	2	13	44	35	6	1	2	2	21							
5	2	14	17	31	6	1	3	69	81							

the packing of molecules within the unit cell. In the 5-formyluracil heterocycle, bond distances and angles are close to the averaged values published by Voet and Rich¹⁸ and in general do not deviate beyond the 3σ limit. The slightly increased exocyclic angle $O(4)-C(4)-C(5)$, 127.5° and the decreased angle $C(3)-C(4)-O(4)$, 117.9° could be due to steric strain between the $C(4) = O(4)$ carbonyl and the formyl group both of which are coplanar with the heterocycle.

In the ribose moiety, bond angles and distances are similar to those averaged for C(3')-endo riboses¹⁹. It should be noted that the bonds to the disordered atom $O(5')$, $C(5')-O(5')$, are shortened with respect to averaged data, presumably owing to excessive thermal motion. The conformation of α -5-formyluridine is of particular interest. In the α -nucleotides summarized previously by Sundaralingam²⁰, the ribose puckering is predominantly C(2')-exo or C(2')-endo or C(3')-endo-C(2')-exo or C(4')-endo-C(3')-exo. In α -5-formyluridine, however, a rather pure C(3')-endo envelope conformation does occur with the angle $C(4')-O(4')-C(1')-C(2')$ at 1.3° . This conformation obviously represents an exceptional case in the realm of α -nucleosides and does not devalue, in our opinion, the finding that the preferred conformations of α -nucleosides are enantiomeric to those of the β -nucleosides²⁰. The conformation about the glycosidic $C(1')-N$ bond is the usual anti but the dihedral angle $C(6)-N(1)-C(1')-O(4')$, -21.6° , is outside the α -nucleoside range of -30° to -72° and corresponds more closely to the (enantiomeric) average, 20° found in β -nucleosides with C(3')-endo sugar puckering.

The orientation of the $C(5')-O(5')$ bond is gauche, gauche for the main sites as in most of the α - and β -nucleosides but gauche, trans and trans, gauche for the minor sites. A similar disorder of the $O(5')$ hydroxyl group was observed in the crystal structure of dihydrouridine²¹. The three $O(5')$ sites are so far from any other potential hydrogen bond donor or acceptor that such intermolecular forces become unlikely for $O(5')$. The disorder of $O(5')$ could be due to this peculiarity which is a result of the crystal packing scheme but could also be discussed in terms of lacking $C(6)-H\cdots O(5')$ interactions. Since in all the α -nucleosides intramolecular (pyrimidine) $C(6)-H\cdots O(5')$ and (purine) $C(8)-H\cdots O(5')$ interactions are not possible, the ratio of structures with gauche, gauche to those with gauche, trans or trans, gauche conformations should give some clue about the impor-

Fig. 3a

Stereo view of α -5-formyluridine molecule along b -axis. Thermal ellipsoids are represented at the 50 % probability level. Note disorder of O(5').

Fig. 3b

A view along the a -axis. Minor sites of atom O(5') omitted. Circles with increasing radius represent H, C, N, O.

Fig. 4

Stereo view showing the packing of α -5-formyluridine molecules in the unit cell.

Fig. 5

The heterocycles are stacked at 3.4 Å distance and show no overlap.

tance of these interactions. Since about 75 % of the α -nucleosides but more than 90 % of the β -nucleosides are gauche, gauche, it is to conclude that this conformation is preferred. Further, the C-H...O(5') interactions are contributing to its stabilization in the β -nucleosides. Sundaralingam²⁰ has discussed the same problem earlier but he found that C-H...O(5') interactions are not involved in the stabilization of the gauche, gauche conformation.

Figure 4 shows a stereoscopic view of the crystal structure down the a-axis. Atoms N(3), O(4), O(7), O(2') and O(3') are making close contacts - the intermolecular distances N(3)-O(4), O(2')-O(7) and O(3')-O(3') being 2.75 Å, 2.74 Å and 3.08 Å respectively. Bond distances N(3)-H(3) = 1.02 Å, H(3)...O(4) = 2.44 Å and angle O(4)-H(3)-O(4) = 158.3° indicates that N(3)-O(4) is probably a hydrogen bond. No comment can be made about the other two close contacts since the hydrogen atoms attached to O(2') and O(3') could not be located. Figure 5, a projection of adjacent molecules on a heterocycle plane, demonstrates that virtually no base overlap is observed in this crystal structure. There might be some dipole-dipole interactions because the (negatively charged) O(7) atom is placed near the (positively charged) C(2) atom.

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