

We are grateful to our colleagues Professor Ernest Eliel and Professor Robert McKee for helpful discussions. This investigation was supported by Public Health Service Research Grant No. CA-15171-02 from the National Cancer Institute.

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## The Crystal and Molecular Structure of 2-Acetamido-2,3-dideoxy-D-threo-hex-2-enono-1,4-lactone, C<sub>8</sub>H<sub>11</sub>NO<sub>5</sub>

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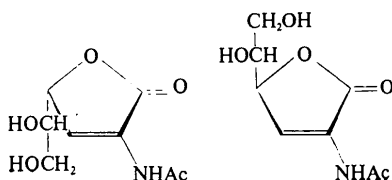
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(Received 19 January 1976; accepted 17 February 1976)

2-Acetamido-2,3-dideoxy-D-threo-hex-2-enono-1,4-lactone crystallizes in the space group  $P2_12_1$  with  $a = 6.178$ ,  $b = 6.925$ ,  $c = 21.523$  Å,  $Z = 4$ . The structure was solved by direct methods and refined to an  $R$  of 0.037. The five-membered lactone ring is planar within experimental error. The molecules are packed into a three-dimensional network by intermolecular O(3)–H···O(5) (2.777), O(4)–H···O(3) (2.854) and N–H···O(1) (3.033 Å) hydrogen bonds.

### Introduction

Treatment of 2-acetamido-2-deoxy-D-aldono-1,4-lactone (aldono = glucono, mannono or galactono) with methanolic KOH gives a mixture of two unsaturated lactones in approximately equal proportions. These two lactones were identified as 2-acetamido-2,3-dideoxy-D-threo-hex-2-enono-1,4-lactone and its D-erythro isomer.



The preparations, the IR and NMR spectral characteristics and the inhibitory activities were described by Pravdić & Fletcher (1971) and Pokorny, Zissis, Fletcher & Pravdić (1975).

The results of the present structure determination of the D-threo isomer confirm the configuration and conformation given by Pravdić & Fletcher (1971).

### Experimental

The space group (Table 1) was determined from Weissenberg photographs recorded with Cu  $K\alpha$  radiation. The diffraction symmetry and space-group extinction determined  $P2_12_1$  uniquely.

The intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer with

Table 1. *Crystallographic and physical data*2-Acetamido-2,3-dideoxy-D-*threo*-hex-2-enono-1,4-lactone,  
C<sub>8</sub>H<sub>11</sub>NO<sub>5</sub>

F.W.	201.18
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 1
<i>a</i>	6.178 (2) Å*
<i>b</i>	6.925 (1)
<i>c</i>	21.523 (8)
<i>U</i>	920.8 Å <sup>3</sup>
<i>D<sub>c</sub></i>	1.451 g cm <sup>-3</sup>
<i>Z</i>	4
$\mu$ (Cu <i>K</i> $\alpha$ )	7.40 cm <sup>-1</sup>
Crystal shape	Prismatic

\* Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

the  $\omega$ -scan mode (scan width = 1.2° $\theta$ , scan speed = 0.04° $\theta$  s<sup>-1</sup>) and graphite-monochromated Cu *K* $\alpha$  radiation. The 832 observed independent reflexions in the range 3 <  $\theta$  < 70° were recorded and only these were used in the calculations. Three standard reflexions were measured every 2h to provide a check on crystal and instrumental stability and showed only the variations expected from counting statistics. The data were corrected for background, Lorentz and polarization effects, but not for absorption or extinction. A correction for monochromator polarization was included.

### Structure determination and refinement

The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). Overall temperature ( $B = 2.49$  Å<sup>2</sup>) and scale factors were determined (Wilson, 1942) and used to compute normalized structure factors by the routine *NORMAL* included in *MULTAN*. The solution was based on 250 reflexions with  $|E| > 1.1$ . The *E* map corresponding to the solution with the best figure of merit revealed the positions of 13 non-hydrogen atoms. The C atom belonging to the methyl group was located from the resulting Fourier synthesis. A full-matrix least-squares procedure mini-

mizing  $\sum w||F_o| - |F_c||^2$  with  $w = 1/\sigma_{F_o}^2$  was used for refinement.

Heavy-atom coordinates, isotropic thermal parameters and a scale factor were refined to an *R* of 0.095. Anisotropic refinement (*R* = 0.068) and a subsequent difference synthesis were applied for the location of the H atoms. In the final cycles one scale factor, the atomic coordinates for all atoms, and anisotropic thermal parameters for the heavy atoms (151 parameters in all) were varied. For H the isotropic thermal parameters are those of the bonded atom. The final residuals were:  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.037$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2} = 0.045$ .

Scattering factors given by Cromer & Mann (1968) and (for H) by Stewart, Davidson & Simpson (1965) were used.

The calculations were carried out on the Univac 1110 computer at the University Computing Centre in Zagreb with the X-RAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Positional and thermal parameters are listed in Tables 2 and 3.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31687 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Positional parameters* ( $\times 10^3$ ) and *isotropic thermal parameters* ( $\times 10^2$ ) for the hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å <sup>2</sup> )
H(3)	119 (7)	1000 (6)	677 (2)	3.6 (1.0)
H(4)	422 (6)	765 (5)	646 (2)	3.4 (1.0)
H(5)	255 (7)	696 (6)	747 (2)	4.7 (1.2)
H(6,1)	513 (8)	472 (7)	702 (2)	5.3 (1.3)
H(6,2)	306 (8)	332 (7)	675 (2)	5.8 (1.3)
H(8,1)	-404 (11)	1224 (10)	512 (3)	10.4 (2.1)
H(8,2)	-419 (13)	1403 (10)	561 (3)	12.5 (2.6)
H(8,3)	-530 (13)	1240 (11)	571 (3)	12.6 (2.9)
H(N)	-251 (7)	969 (6)	538 (2)	3.8 (1.1)
H(O3)	-44 (9)	472 (8)	684 (2)	7.4 (1.7)
H(O4)	210 (10)	274 (9)	771 (3)	10.7 (2.2)

Table 2. *Final positional* ( $\times 10^4$ ) and *thermal parameters* ( $\times 10^3$ ) for non-hydrogen atoms

$$T = \exp [-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \dots + 2U_{23}klb^*c^*)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
C(1)	418 (6)	7122 (5)	5613 (1)	37 (2)	28 (2)	30 (2)	2 (2)	3 (1)	-1 (1)
C(2)	-122 (6)	8931 (5)	5943 (1)	35 (2)	25 (2)	29 (2)	1 (2)	1 (1)	1 (1)
C(3)	1145 (7)	9083 (5)	6437 (2)	47 (2)	25 (2)	32 (2)	-3 (2)	-4 (2)	0 (1)
C(4)	2537 (6)	7329 (6)	6481 (2)	36 (2)	32 (2)	34 (2)	0 (2)	-5 (1)	-2 (1)
C(5)	2098 (6)	6142 (5)	7069 (2)	32 (2)	27 (2)	34 (2)	-1 (2)	-5 (2)	0 (1)
C(6)	3499 (6)	4351 (6)	7104 (2)	37 (2)	33 (2)	49 (2)	2 (2)	-1 (2)	6 (2)
C(7)	-2240 (7)	11897 (5)	5900 (2)	43 (2)	26 (2)	34 (2)	1 (2)	0 (2)	-4 (1)
C(8)	-4033 (10)	12868 (8)	5553 (3)	55 (3)	43 (3)	63 (3)	18 (2)	-9 (3)	-8 (2)
O(1)	-304 (5)	6512 (4)	5132 (1)	60 (2)	40 (1)	31 (1)	8 (2)	-4 (1)	-12 (1)
O(2)	1971 (4)	6186 (4)	5935 (1)	41 (2)	33 (1)	31 (1)	8 (1)	1 (1)	-3 (1)
O(3)	-145 (4)	5655 (3)	7117 (1)	31 (1)	28 (1)	35 (1)	-1 (1)	0 (1)	-4 (1)
O(4)	3432 (5)	3495 (5)	7704 (1)	42 (2)	46 (2)	58 (2)	1 (2)	-11 (1)	21 (1)
O(5)	-1240 (5)	12642 (4)	6326 (1)	68 (2)	32 (1)	47 (1)	1 (2)	-16 (2)	-13 (1)
N	-1761 (6)	10069 (4)	5700 (1)	43 (2)	28 (2)	32 (1)	4 (1)	-8 (1)	-9 (1)

Table 4. Bond angles ( $^{\circ}$ )

O(1)—C(1)—O(2)	122.4 (3)	C(6)—C(5)—H(5)	104 (2)
O(1)—C(1)—C(2)	128.8 (3)	O(4)—C(6)—C(5)	111.7 (3)
O(2)—C(1)—C(2)	108.7 (3)	O(4)—C(6)—H(6,1)	106 (2)
C(1)—C(2)—C(3)	108.6 (3)	O(4)—C(6)—H(6,2)	111 (2)
C(1)—C(2)—N	117.8 (3)	C(5)—C(6)—H(6,1)	110 (2)
C(3)—C(2)—N	133.5 (3)	C(5)—C(6)—H(6,2)	111 (3)
C(2)—C(3)—C(4)	109.1 (3)	H(6,1)—C(6)—H(6,2)	107 (3)
C(2)—C(3)—H(3)	132 (2)	O(5)—C(7)—C(8)	124.0 (4)
C(4)—C(3)—H(3)	119 (2)	O(5)—C(7)—N	121.2 (4)
O(2)—C(4)—C(3)	104.6 (3)	C(8)—C(7)—N	114.8 (4)
O(2)—C(4)—C(5)	109.4 (3)	C(7)—C(8)—H(8,1)	106 (4)
C(3)—C(4)—C(5)	112.8 (3)	C(7)—C(8)—H(8,2)	117 (5)
O(2)—C(4)—H(4)	108 (2)	C(7)—C(8)—H(8,3)	107 (5)
C(3)—C(4)—H(4)	113 (2)	H(8,1)—C(8)—H(8,2)	123 (6)
C(5)—C(4)—H(4)	109 (2)	H(8,1)—C(8)—H(8,3)	101 (6)
O(3)—C(5)—C(4)	110.9 (3)	H(8,2)—C(8)—H(8,3)	101 (7)
O(3)—C(5)—C(6)	110.9 (3)	C(2)—N—C(7)	124.5 (3)
C(4)—C(5)—C(6)	112.2 (3)	C(2)—N—H(N)	121 (3)
O(3)—C(5)—H(5)	109 (2)	C(7)—N—H(N)	114 (3)
C(4)—C(5)—H(5)	109 (2)	C(1)—O(2)—C(4)	108.8 (3)

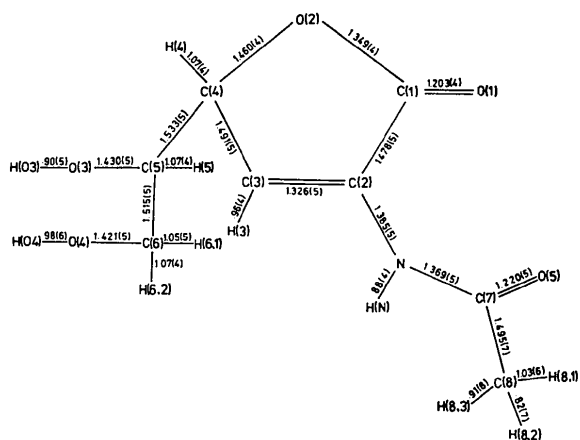


Fig. 1. The numbering of the atoms and bond lengths.

## Description and discussion of the structure

The numbering of the atoms and the bond lengths are shown in Fig. 1. Molecular packing and hydrogen bonds are illustrated in Fig. 2. Interatomic angles are listed in Table 4, displacements of the atoms from the least-squares planes through the lactone group and ring in Table 5. Dihedral angles defining the conformation about C(4)—C(5) and C(5)—C(6) are given in Table 6.

Table 5. Displacements from least-squares planes ( $\text{\AA}$ )

Atoms included in the calculation of least-squares planes are denoted by an asterisk.

Lactone group			
C(2)*	0.002	O(2)*	0.009
C(1)*	0.008	C(4)*	-0.010
O(1)*	-0.010		
Lactone ring			
C(1)*	-0.007	O(1)	-0.048
C(2)*	0.014	N	0.070
C(3)*	-0.014	H(3)	0.050
C(4)*	0.009	H(4)	-0.856
O(2)*	-0.001	C(5)	1.265

Table 6. Dihedral angles describing the conformation about C(4)—C(5) and C(5)—C(6)

C(3)—C(4)—C(5)—O(3)	54.4 (4) $^{\circ}$
C(3)—C(4)—C(5)—H(5)	-65 (2)
O(2)—C(4)—C(5)—O(3)	-61.5 (4)
O(2)—C(4)—C(5)—C(6)	63.3 (4)
H(4)—C(4)—C(5)—C(6)	-55 (2)
H(4)—C(4)—C(5)—H(5)	61 (3)
C(4)—C(5)—C(6)—H(6,1)	49 (2)
C(4)—C(5)—C(6)—H(6,2)	-68 (3)
O(3)—C(5)—C(6)—O(4)	-68.0 (4)
O(3)—C(5)—C(6)—H(6,2)	56 (3)
H(5)—C(5)—C(6)—O(4)	49 (2)
H(5)—C(5)—C(6)—H(6,1)	-69 (3)

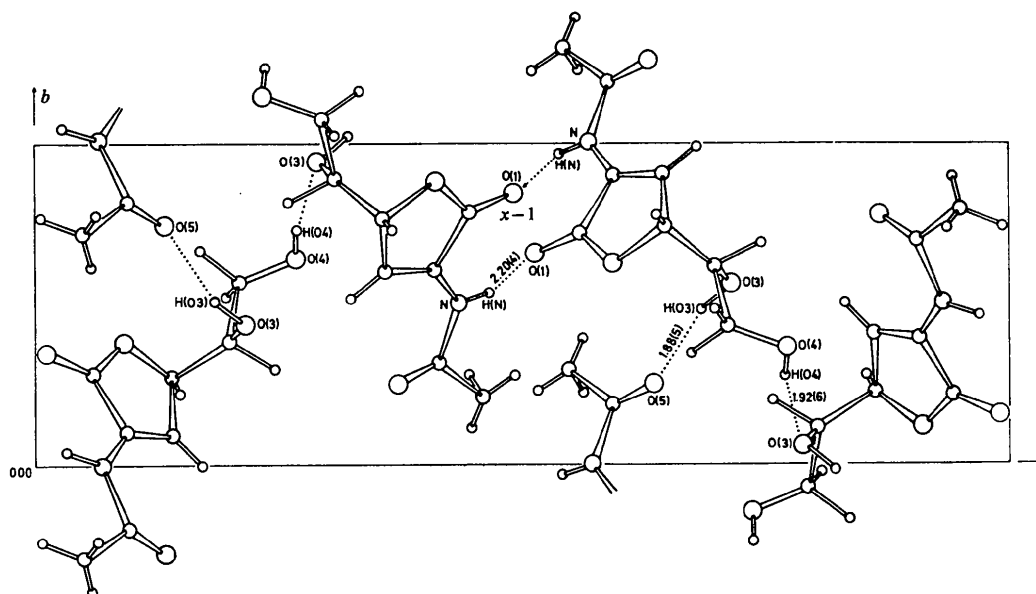


Fig. 2. A view of the crystal structure along a showing the packing arrangement and hydrogen bonds.

Table 7. *Hydrogen bonds*

$X-H \cdots Y$	$X \cdots Y$	$X-H$	$H \cdots Y$	$\angle X-H \cdots Y$	Symmetry operation
$O(3)-H(O3) \cdots O(5)$	2.777 (4) Å	0.90 (5) Å	1.88 (5) Å	174 (4)°	$x, y, z; x, y-1, z$
$O(4)-H(O4) \cdots O(3)$	2.854 (4)	0.98 (6)	1.92 (6)	160 (5)	$x, y, z; \bar{x}, (\frac{1}{2} + y) - 1, (\frac{1}{2} - z) + 1$
$N-H(N) \cdots O(1)$	3.033 (4)	0.88 (4)	2.20 (4)	157 (3)	$x, y, z; (\frac{1}{2} + x) - 1, (\frac{1}{2} - y) + 1, 1 - z$

The C=C(=O)-O-C group and the lactone ring are both planar within experimental error (Table 5). The bond lengths and angles [with the exception of the internal angles at C(2) and C(3)] are generally comparable to the values expected for the type of hybridization and also with those found in L-ascorbic acid (Hvoslef, 1968). C(4)-C(5) 1.533 (5) and C(5)-C(6) 1.515 (5) Å are in agreement with the value for a C-C single bond. C(2)=C(3) 1.326 (5) is comparable to 1.337 (6) Å (*International Tables for X-ray Crystallography*, 1968). The single bonds C(1)-C(2) [1.478 (5)] and C(3)-C(4) [1.491 (5) Å] are shortened due to the presence of C=O and C=C double bonds. The single and double C-O bonds are in the usual range, but the endocyclic C(1)-O(2) [1.349 (4)] and C(4)-O(2) [1.460 (4) Å] are asymmetric with well pronounced differences from the normal C-O single bond of 1.428 Å (Sundaralingam, 1968). The same effect was observed in, e.g. L-ascorbic acid (Hvoslef, 1968) and  $\gamma$ -D-gulonolactone (Berman, Rosenstein & Southwick, 1971). The internal angles in the five-membered ring have a mean value of 107.9° with the largest deviations in the angles about C(2)=C(3) [108.6 (3)] and [109.1 (3)°]. The endocyclic valence angles are in good agreement with the values in L-ascorbic acid (Hvoslef, 1968), the same distortions occurring in the angles about the double bond. The ring O valence angle of 108.8 (3)° is near to the tetrahedral value.

The molecular packing is dominated by three independent intermolecular hydrogen bonds (Fig. 2 and Table 7). Both hydroxyl groups are involved in O(4)-H...O(3), 2.854 (4) Å, hydrogen bonds. The O(3) hydroxyl group is hydrogen-bonded to the carbonyl

group by O(3)-H...O(5) of 2.777 (4) Å. The nitrogen atom in the acetamido group acts as a donor to the carbonyl O forming the N-H...O(1), 3.033 (4) Å, hydrogen bond.

The intensities were collected at the Department of General and Inorganic Chemistry, Faculty of Science, University of Zagreb. The authors thank Mr Milenko Bruvo for collecting the data. Thanks are due to Dr N. Pravić for the crystals used in this study and for valuable discussion.

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