

The Crystal and Molecular Structure of D-Arabeto- γ -lactone

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Abstract

$C_5H_8O_5$ is orthorhombic, space group $P2_12_12_1$, with $a = 11.797$ (3), $b = 10.907$ (3), $c = 4.769$ (1) Å, $Z = 4$. The structure was refined to $R = 0.030$ for 1044 counter reflections with $I > 2\sigma(I)$. The molecular parameters are in good agreement with those found in similar structures. The atoms of the lactone group are within ± 0.053 Å of the least-squares plane of the group.

Introduction

D-Arabeto- γ -lactone has been identified as a metabolic product in the degradation of D-arabinose in the bacteria *Penicillium saccharofila* (Paleroni & Douderoff, 1957). The molecule is also a competitive inhibitor of a specific glycosidase (Kanfer & Spielvogel, 1973). Two other γ -lactones of D-aldoses, containing one furanose ring, have been determined (Fig. 1,

GALA and GULO), special interest being paid to the data of the lactone group. A trimethyl derivative of GALA (*i.e.* MGALA) has also been determined. The main difference between D-arabeto- γ -lactone (ARA) and the structures above is in the side chain attached at position 5, which in ARA is the same as that found in methyl α -D-lyxofuranoside (LXFU). In Fig. 1 is also shown the related structure of the biologically important L-ascorbic acid (vitamin C) (ASCA).

Experimental

Crystal data

A crystal $0.2 \times 0.4 \times 0.6$ mm was selected from a commercial sample (Koch-Light Laboratories, Ltd) after recrystallization from ethanol. The crystal was mounted on a glass fibre with c approximately parallel to the ϕ axis of the goniometer. The crystal was mounted on a Picker FACS-I four-circle automatic diffractometer, and the lattice parameters were determined by least squares from the setting angles of 24 reflections from different parts of reciprocal space. The final lattice parameters were taken as the average of the values found in four refinements before, during and after data collection, with *e.s.d.*'s equal to the largest ones determined by a single refinement (Svinning, 1978). The data are summarized in Table 1.

Data collection and processing

Two equivalent sets (hkl and $\bar{h}\bar{k}l$) (a and b , respectively) of intensities were measured with Nb-

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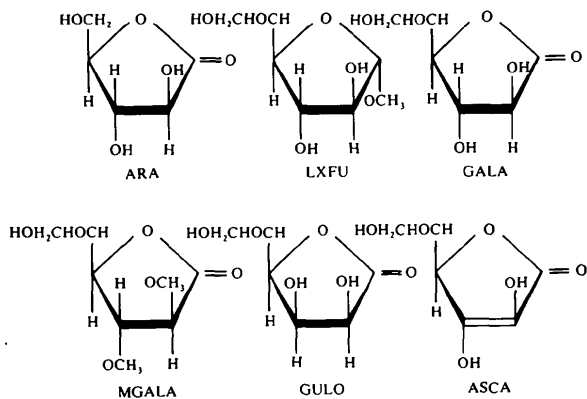


Fig. 1. The structures of selected γ -lactones and similar molecules (see text): ARA: arabeto- γ -lactone (present work); LXFU: methyl α -D-lyxofuranoside (Groth & Hammer, 1968); GALA: D-galactono- γ -lactone (Jeffrey, Rosenstein & Vlasse, 1967); MGALA: 2,3,6-trimethylgalactono- γ -lactone (Sheldrick, 1973); GULO: γ -D-gulonolactone (Berman, Rosenstein & Southwick, 1971); ASCA: L-ascorbic acid (Hvoslef, 1968).

Table 1. Crystal data of arabeto- γ -lactone with *e.s.d.*'s in parentheses

Chemical formula:	$C_5H_8O_5$
Formula weight:	148
$F(000) = 312$	
$a = 11.797$ (3), $b = 10.907$ (3), $c = 4.769$ (1) Å	
Systematic absences:	$h00: h = 2n + 1, 0k0: k = 2n + 1,$ $00l: l = 2n + 1$
Space group:	$P2_12_12_1$
$V = 613.59$ Å ³	
$D_c = 1.25$ Mg m ⁻³ for $Z = 4$	
$\lambda(\text{Mo } K\alpha) = 0.71073$ Å	
$\mu = 0.13723$ mm ⁻¹	

filtered Mo $K\alpha$ radiation from one crystal. The diffractometer was equipped with a scintillation counter and a pulse-height analyser. A recovery constant for the counting system was determined by a modification of the method of Sletten, Sletten & Jensen (1969). An $\omega/2\theta$ scan mode with a speed of 2° min^{-1} was applied. The background was measured for 20 s at each end of the scan, and three standard reflections were measured after each 50 reflections. The low-angle reflections influenced by the Nb absorption edge were remeasured with a narrower scan width on the low-angle side of the peak. The standard intensities decreased by 3% during data collection.

The data were corrected for Lorentz and polarization factors, coincidence loss and long-range variations. The recovery constant, τ' , was estimated to be $9.034 \times 10^{-8} \text{ counts}^{-1}$ and the integrated intensities were corrected by the expression $I = I_o / (1 - \tau'I_o)$, where I_o is the observed intensity. Corrections for long-range variations were performed by fitting polynomials to a plot of the normalized average intensity of the standard reflection group as a function of the reflection number. The data were not corrected for absorption. The absorption correction factor ranged from 1.010 to 1.022 (F scale). The average intensities were calculated for equivalent reflections of sets a and b . A discrepancy index defined as $D = (\sum_{j=1}^n |F_{1j}^2 - F_{2j}^2|) / \sum_{j=1}^n \bar{F}^2$, the summation being taken over all reflections, was 0.0168.

Structure solution and refinement

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and *TANGEN* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Isotropic

Table 2. *Positional parameters of arabono- γ -lactone*

The x , y and z fractional coordinates have been multiplied by 10^4 for C and O, and by 10^3 for H.

	x	y	z
C(1)	2826 (2)	2664 (2)	1207 (6)
O(2)	2363 (1)	3765 (1)	1693 (5)
C(3)	1444 (2)	3652 (2)	3773 (6)
C(4)	533 (2)	4573 (2)	3073 (7)
C(5)	1137 (2)	2285 (2)	3641 (5)
O(6)	600 (2)	1924 (2)	6162 (5)
C(7)	2307 (2)	1737 (2)	3179 (5)
O(8)	2345 (2)	543 (2)	2060 (4)
O(9)	3528 (2)	2493 (2)	-595 (4)
O(10)	135 (2)	4494 (2)	261 (5)
H(31)	173 (2)	384 (3)	569 (7)
H(41)	88 (2)	542 (2)	329 (7)
H(42)	-12 (3)	451 (3)	450 (8)
H(51)	68 (2)	213 (2)	202 (5)
H(61)	37 (3)	110 (4)	599 (10)
H(71)	276 (2)	179 (3)	503 (9)
H(81)	245 (4)	13 (4)	321 (8)
H(101)	-30 (3)	391 (3)	15 (9)

least-squares refinement of the non-hydrogen atoms based on 1044 observed reflections gave $R = 0.11$. After anisotropic refinement R dropped to 0.06, and all the H atoms were found from ΔF maps. The C, N and O atoms were refined anisotropically and the H atoms isotropically to a final R of 0.030 ($R_w = 0.032$). The weights were of the type $\sigma^{-1}(F_{\text{obs},h})$. The χ^2 parameter (Bevington, 1969) was 2.58, and there was no parameter shift greater than 0.002 times the e.s.d.* The final ΔF map had no areas of residual electron density outside the range -0.13 to $+0.26 \text{ e } \text{Å}^{-3}$. All least-squares and Fourier calculations were made with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Results and discussion

Final positional parameters are given in Table 2, bond lengths and angles in Table 3.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34712 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths (Å) and angles (°) not involving H atoms*

E.s.d.'s are in parentheses.

	SS	AV*	AVS*
C(1)—O(2)	1.339 (3)	1.352 (5)	3, 4, 5, 6
C(1)—C(7)	1.510 (3)	1.520 (5)	3, 4, 5
C(1)—O(9)	1.208 (3)	1.203 (10)	3, 4, 5, 6
O(2)—C(3)	1.475 (3)	1.457 (11)	2, 3, 4, 5, 6
C(3)—C(4)	1.508 (4)	1.503 (4)	2
C(3)—C(5)	1.535 (3)	1.528 (14)	2, 3, 4, 5
C(4)—O(10)	1.423 (4)	1.430 (4)	2
C(5)—O(6)	1.415 (3)	1.415 (4)	2, 3, 5
C(5)—C(7)	1.521 (4)	1.523 (7)	2, 3, 4, 5
C(7)—O(8)	1.409 (3)	1.405 (3)	2, 3, 4, 5
O(2)—C(1)—C(7)	109.1 (2)	109.5 (2)	3, 4, 5, 6
O(2)—C(1)—O(9)	122.7 (2)	121.8 (4)	3, 4, 5, 6
C(7)—C(1)—O(9)	128.1 (2)	128.5 (4)	3, 4, 5, 6
C(1)—O(2)—C(3)	109.9 (2)	109.3 (6)	2, 3, 4, 5, 6
O(2)—C(3)—C(4)	108.6 (2)	109.9 (6)	2, 3, 4, 6
O(2)—C(3)—C(5)	103.1 (2)	103.9 (7)	2, 3, 4, 5, 6
C(4)—C(3)—C(5)	118.0 (2)	115.1 (9)	2, 3, 4, 5, 6
C(3)—C(4)—O(10)	113.8 (2)	111.1 (2)	2
C(3)—C(5)—O(6)	109.9 (2)	108.6 (8)	2, 3, 4, 5
C(3)—C(5)—C(7)	100.0 (2)	100.3 (6)	2, 3, 4, 5
O(6)—C(5)—C(7)	114.8 (2)	113.2 (32)	2, 3, 4, 5
C(1)—C(7)—C(5)	101.3 (2)	102.1 (6)	2, 3, 4, 5
C(1)—C(7)—O(8)	111.7 (2)	112.8 (9)	2, 3, 4, 5
C(5)—C(7)—O(8)	116.5 (2)	113.3 (10)	2, 3, 4, 5

* The values in column AV are the averages of the structures identified in column AVS: 2: LXFU, 3: GALA, 4: MGALA, 5: GULO, 6: ASCA. Values in column SS refer to this work.

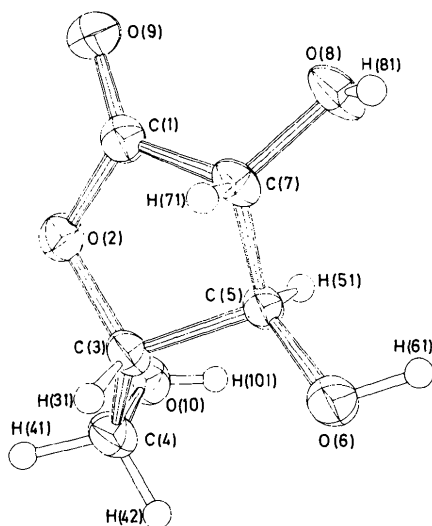


Fig. 2. Atom numbering and ORTEP (Johnson, 1976) drawing of ARA.

Bond lengths and angles

The most significant differences between bond lengths of arabono- γ -lactone and the mean of corresponding bonds in the structures illustrated in Fig. 1 were *ca* 4σ for C(1)–O(2) and *ca* 6σ for O(2)–C(3) (Table 3 and Fig. 2). However, the differences are 2σ and 1σ when only the structure of GULO is considered ($R_{\text{GULO}} = 0.039$, $R_{\text{GALA}} = 0.078$, $R_{\text{MGALA}} = 0.102$). These bonds have been discussed by Mo & Sivertsen (1971) who found 1.348 and 1.443 Å in an analysis of the γ -lactone of 2-butenic acid. The average —C—OH bond is 1.416 (7) Å and the average

—C—C— bond is 1.521 (14) Å. The shortening of C(3)–C(4) may be due to a rehybridization of C caused by the neighbouring O atoms (*cf.* Svinning, Mo & Bruun, 1976). The average C–H and O–H bonds are 1.01 (3) and 0.83 (11) Å respectively.

The internal angles of the lactone ring are all within 2σ of the average values (Table 3). The largest deviations are found among the external angles at C(3), C(5) and C(7) and may be influenced by the differences in environments (*i.e.* the side chains and the molecular packing).

Molecular structure and packing

The atoms of the lactone group C(7)–C(1) [=O(9)]–O(2)–C(3) are within ± 0.053 Å of their least-squares plane (Table 4). The deviation from planarity is larger for ARA than for GULO (± 0.01 Å) and GALA (± 0.03 Å). The χ^2 value [*i.e.* $\sum_{m=1}^n d_m^2 / \sigma_{\text{ref}}^2$, where d_m is the deviation from the least-squares plane and σ_{ref}^2 is the

Table 4. Least-squares plane of the lactone group and deviations from this plane

E.s.d.'s are 1×10^{-3} Å for all atoms. x, y, z are orthogonal axes of length 1 Å parallel to a, b and c , respectively.

Plane equation: $0.6951x + 0.2149y + 0.6861z = 3.3212$.

	Deviation from the plane (Å)		Deviation from the plane (Å)
C(3)	–0.047	C(5)*	–0.662
O(2)	0.053	O(8)*	–0.598
C(1)	0.015	O(6)*	–0.362
O(9)	–0.039	C(4)*	–0.807
C(7)	0.018	O(10)*	–2.072

* Atoms not defining the plane.

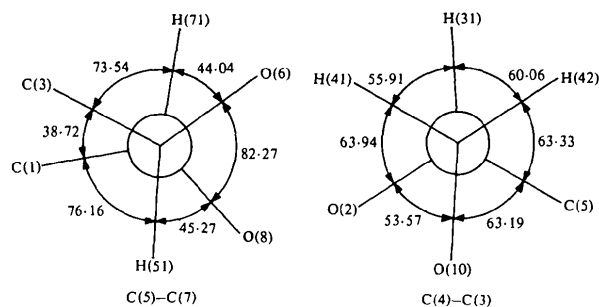


Fig. 3. Newman projections showing the conformations about C(5)–C(7) and C(4)–C(3). E.s.d.'s are $0.10\text{--}0.20^\circ$.

Table 5. The hydrogen-bonding data (*cf.* Hamilton & Ibers, 1968)

E.s.d.'s are 1×10^{-2} Å. Symmetry operations are as in Table 6.

Donor <i>D</i>	Acceptor <i>A</i>	Distances	
		<i>D</i> – <i>A</i>	H– <i>A</i>
O(8)	O(8 ^{vi})	2.69 Å	1.99 Å
O(10 ^{ix})	O(9)	2.88	2.07
O(6 ^{xiii})	O(10)	2.87	1.95

mean-square value of $\sigma_{x,y,z}$; *cf.* Stout & Jensen (1968)] calculated for the lactone group is 1263 for $n - 3 = 2$ degrees of freedom, *i.e.* the lactone group is not strictly planar within experimental error. The fifth atom of the ring, C(5), is 0.66 Å away from the plane. The corresponding value for GULO was 0.58 Å, and for GALA 0.64 Å. The deviation is presumed to be caused by a repulsion between the hydroxyl groups attached to C(5) and C(7) (Berman, Rosenstein & Southwick, 1971). The resulting conformation is shown in Fig. 3. The torsion angle O(6)–C(5)–C(7)–O(8) is 82.3° . The conformation about C(4)–C(3) is similar to that about the C(5)–C(4) bond of GALA.

Table 6. Intermolecular distances (\AA) less than 0.2 \AA + sum of the van der Waals radii (Kitaigorodskii, 1973), excluding hydrogen bonds

E.s.d.'s are 1×10^{-2} \AA or less.

The symmetry transformations of the second atom are:

(i)	$x,$	$y,$	$1+z$	(ix)	$\frac{1}{2}+x,$	$\frac{1}{2}-y,$	$-z$
(iv)	$\frac{1}{2}-x,$	$1-y,$	$\frac{1}{2}+z$	(xiii)	$-x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z.$
(vi)	$\frac{1}{2}-x,$	$-y,$	$\frac{1}{2}+z$				
C(3)...	O(2 ^{iv})	3.44		O(9)...	C(4 ^{ix})	3.47	
C(4)...	O(2 ^{iv})	3.53		O(9)...	C(5 ^{ix})	3.41	
C(4)...	O(9 ^{iv})	3.45		O(9)...	H(51 ^{ix})	2.66	
C(4)...	O(10 ⁱ)	3.46		O(10)...	C(5 ^{xiii})	3.43	
C(4)...	O(6 ^{xiii})	3.53		H(31)...	O(2 ^{iv})	2.86	
C(4)...	C(5 ^{xiii})	3.65		H(41)...	C(1 ^{iv})	2.94	
C(4)...	H(51 ^{xiii})	3.14		H(41)...	O(2 ^{iv})	2.77	
C(4)...	H(61 ^{xiii})	2.77		H(42)...	O(10 ⁱ)	2.76	
C(7)...	O(9 ^{iv})	3.40		H(71)...	C(1 ⁱ)	3.10	
C(7)...	O(8 ^{iv})	3.13		H(71)...	O(9 ^{iv})	2.40	
C(7)...	H(81 ^{vi})	3.16		H(71)...	O(8 ^{vi})	2.72	
O(6)...	H(51 ⁱ)	2.80		H(81)...	C(7 ^{vi})	3.14	
				H(101)...	H(61 ^{xiii})	2.46	

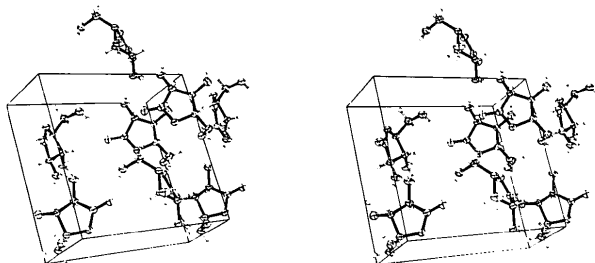


Fig. 4. The molecular packing of arabono- γ -lactone.

The hydrogen-bond data are summarized in Table 5. O(8) and O(10) act as both donors and acceptors. The hydrogen bonds involve three of the molecules in the unit cell; to the fourth (symmetry operation iv) there are two C—O contacts slightly longer than the sum of the van der Waals radii. These and other short intermolecular distances are given in Table 6. The molecular packing of arabono- γ -lactone is shown in Fig. 4.

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