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THE CRYSTAL STRUCTURE OF D-RIBONO-1,4-LACTONE AT −150°

YUKIO KINOSHITA, JOHN R. RUBLE, AND GEORGE A. JEFFREY
Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260 (U.S.A.)
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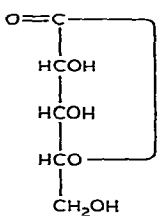
ABSTRACT

The crystal structure of D-ribono-1,4-lactone, **1**, $C_5H_8O_5$, at −150° is orthorhombic, $P2_12_12_1$, with $a = 10.441(2)$, $b = 11.948(3)$, $c = 4.781(1)$ Å, $V = 596.43$ Å (MoKα_1, $\lambda = 0.7107$ Å), $Z = 4$, $D_m = 1.626$ g cm^{-3} (20°), and $D_x = 1.649$ g cm^{-3} (−150°). The 1,4-lactone ring has a conformation midway between E_3 and $^2T_3$, with puckering comparable to that observed in the furanose rings of nucleosides. The C-O-C=O group has bond lengths of 1.467(1), 1.354(1), and 1.203(1) Å, respectively, and is slightly non-planar, with a C-O-C=O torsion angle of 172.7°. The molecules are linked by hydrogen bonds, which form chains. The carbonyl oxygen atom is involved in a weak, bifurcated hydrogen-bond interaction.



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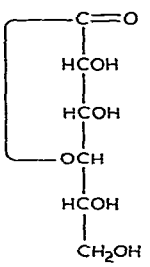

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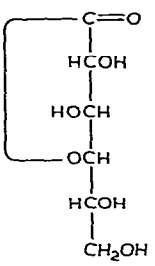

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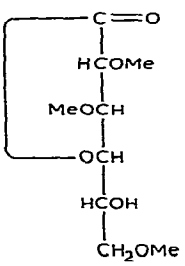

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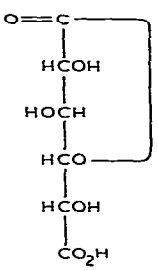

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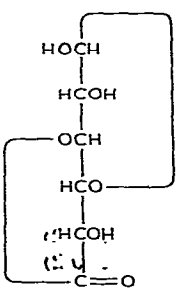

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INTRODUCTION

The crystal structures of six simple γ-lactones have been studied. These are this structure (**1**), D-gulono-1,4-lactone[1] (**2**), D-galactono-1,4-lactone[2] (**3**), 2,3,6-tri-*O*-methyl-D-galactono-1,4-lactone[3] (**4**), D-glucaro-1,4-lactone[4] (**5**), and β-D-glucurono-6,3-lactone[5] (**6**).

Comparison of these results provides information relating to the geometrical characteristics of the γ-lactone ring system and to what degree this can be distorted by crystal-field effects.

EXPERIMENTAL

D-Ribono-1,4-lactone **1**, D-ribonic γ-lactone, CAS No. 5336-08-3, from Vega Biochemicals, was recrystallized from 80% ethanol–water at room temperature. A crystal 0.31 × 0.37 × 0.55 mm was used to measure 2786 symmetry-independent intensities at −150°, using MoKα graphite-monochromated radiation on a CAD-4 diffractometer. Of these, 2418 had values $\geqslant 2\sigma_c$, based on counting statistics. No corrections were made for absorption ($\mu_{\mathrm{MoK}\alpha} = 1.616$) or extinction. The unit-cell parameters were determined by least-squares fit of $\sin^2\theta$ values for 40 reflections with $36° \leqslant 2\theta \leqslant 43°$.

TABLE I

FRACTIONAL ATOMIC COORDINATES[a] FOR D-RIBONO-1,4-LACTONE AT −150°

	x	y	z
C-1	33736(7)	9747(6)	32129(18)
C-2	36756(7)	15508(6)	59463(17)
C-3	51039(7)	17848(6)	56326(19)
C-4	55262(7)	7195(6)	40785(19)
C-5	58512(8)	−2578(7)	59720(20)
O-1	23781(6)	9697(5)	19457(15)
O-2	28616(6)	24733(5)	63223(15)
O-3	52498(6)	27441(5)	39194(19)
O-4	44336(6)	4396(5)	22790(14)
O-5	64710(6)	−11410(5)	44691(16)
H-2	356(1)	102(1)	734(4)
H-3	558(1)	186(1)	723(4)
H-4	623(1)	86(1)	280(3)
H-51	507(1)	−55(1)	683(3)
H-52	648(1)	2(1)	735(3)
H-O-2	306(2)	288(1)	773(4)
H-O-3	598(2)	287(1)	364(4)
H-O-5	590(2)	−144(1)	356(4)

[a]Values are × 10^5 for non-hydrogen atoms, × 10^3 for hydrogen atoms. Estimated standard deviations given in parentheses refer to the least-significant digit.

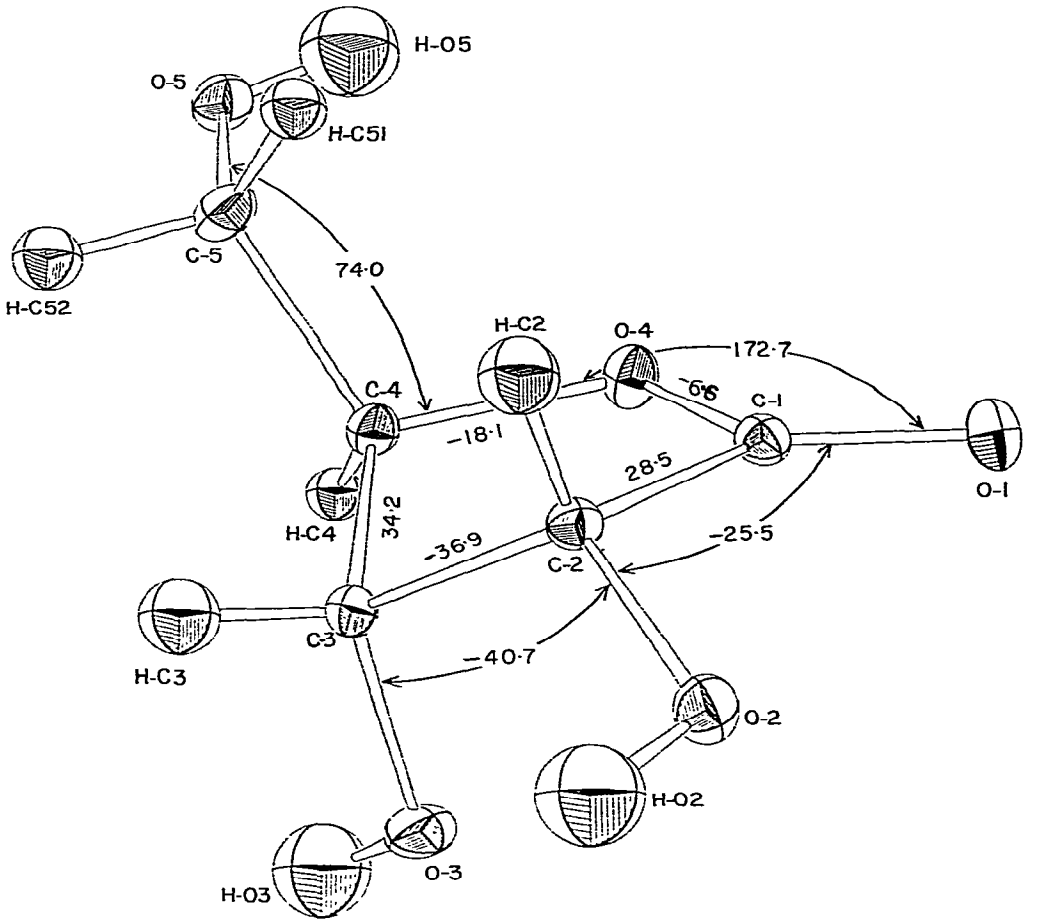


Fig. 1. D-Ribono-1,4-lactone at −150°C. Atomic notation and thermal ellipsoids at 50% probability[16]. The numerical values refer to torsion angles (°). E.s.d. values are 0.1°.

The structure was solved with MULTAN[6], using 106 reflections for phase generation. The first E-map showed all of the non-hydrogen atoms. The hydrogen atoms were located on difference maps at R = 0.092. The parameter refinement was by full-matrix, least squares of $\sum\omega(|F_o| - |F_c|)^2$, where $\omega^{-1} = \sigma^2(F_o) + (0.02I)^2$, using ORFLS[7] with anisotropic parameters for non-hydrogen atoms and isotropic thermal-parameters for hydrogen atoms. The final agreement factors were R = 0.035, $R_\omega = 0.037$, S = 1.59, where $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_\omega = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2}$, and $S = (\sum\omega(|F_o| - |F_c|)/(m - n)^{1/2}$; m is the number of observations and n is the number of variable parameters. The atomic scattering-factors used for carbon and oxygen were those of Doyle and Turner[8] and for hydrogen those of Stewart, Davidson, and Simpson[9]. The atomic parameters are given in Table I.

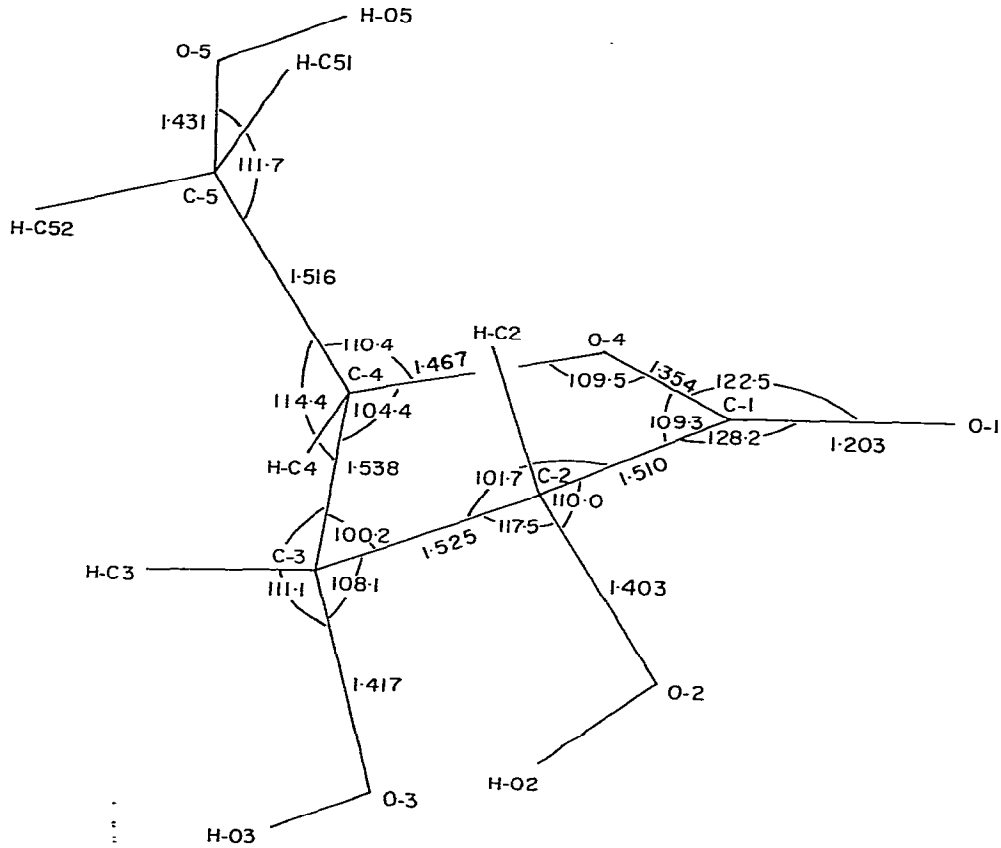


Fig. 2. Bond lengths (Å) and valence angles (°) in D-ribono-1,4-lactone at −150°C. E.s.d. values are 0.001 Å and 0.1°.

The atomic notation and thermal ellipsoids are shown in Fig. 1 and the molecular dimensions are given in Fig. 2*.

DISCUSSION

Because the (C-O-C=O) group is planar, or close to planar, the γ-lactone ring
|
C

is constrained to have a conformation[10] close to E_3, this being less strained than the planar lactone ring. The data in Table II show ring conformations ranging from midway between ${}^2T_3$ ($\varphi = 90°$) through E_3 ($\varphi = 108°$) to midway to ${}^4T_3$ ($\varphi = 126°$).

*Tables of structure factors and anisotropic thermal-parameters are deposited with and can be obtained from: Elsevier Scientific Publishing Company, BBA Data Deposition, P. O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/176/*Carbohydr. Res.*, 92 (1981) 1–7.

The puckering ranges from q = 0.32 to 0.39 Å, a similar range to that observed in the furanose rings of nucleosides. The exception is **6**, where the fused furanose ring constrains the lactone ring to an E_2 conformation (φ = 252°) with less puckering. There are small deviations from planarity of the C–O–C=O group, as measured by the

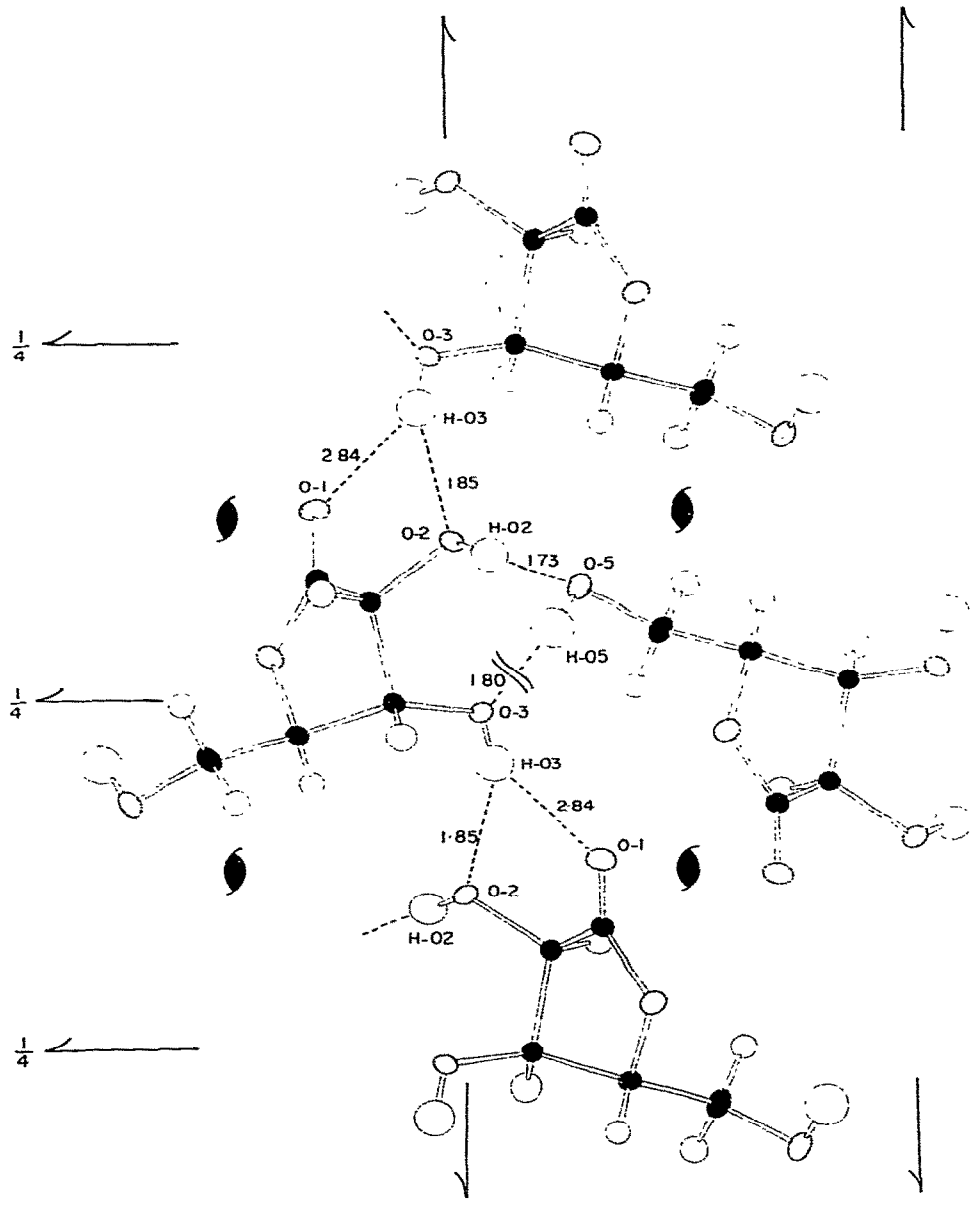


Fig. 3. Hydrogen bonding in the crystal structure of D-ribono-1,4-lactone. The values are H···O hydrogen-bond distances, where the O–H covalent-bond distances are normalized to 0.97 Å in the direction of the O–H bond.

TABLE II

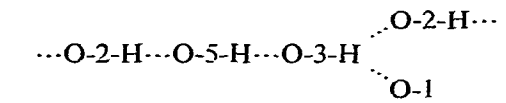
PUCKERING PARAMETERS[a] AND C–O BOND-LENGTHS FOR SOME 1,4-LACTONE RINGS

CRYST File name[b]	*Puckering parameters*		*Bond lengths (Å)*			*Torsion angle (deg)*
	φ(deg)	*q(Å)*	*C-1–O-1*	*C-1–O-4*	*C-4–O-4*	*C-4–O-4–C-1–O-1*
This structure 1	99	0.38	1.203(1)	1.354(1)	1.467(1)	+172.7
GULONO 2	107	0.38	1.194(3)	1.346(3)	1.473(3)	+178.4
GALLAD 3	113	0.39	1.198(5)	1.358(5)	1.464(5)	−178.6
MGALAC 4	104	0.37	1.205(5)	1.350(5)	1.455(6)	+174.7
DGLACM 5	102	0.32	1.210(5)	1.337(4)	1.466(4)	+175.4
GLULAD 6	254	0.16	1.215(5)	1.340(5)	1.475(5)	−169.4

[a]Ref. 14. [b]The six-letter acronym is the REFCODE for searching the Cambridge Crystallographic Data File[15].

C–O–C=O torsion angles. These are presumably due to crystal-field forces, except in the case of **6**, where a larger departure from planarity can be associated with the strain arising from the fused-ring structure. The C–O–C=O bond lengths show the characteristic lengthening and shortening of the formal C–O bonds because of contributions from the valence-bond resonance form $C^{+}–O=C–O^{-}$. The small differences in bond lengths are probably not significant, as they do not appear to be related in any systematic way to the small differences in conformation. The C–C bond lengths are normal, ranging from 1.510 to 1.538 Å, as are the C–OH bonds, 1.403 to 1.431 Å. The orientation of the primary alcohol group is *gauche/trans*.

The hydrogen-bonding scheme is shown as follows.



As in the crystal structure of 1,6-anhydro β-D-galactopyranose[11], the cooperative effect of the infinite chain of hydrogen bonds is maintained while the non-hydrogenated oxygen atom, O-1, is incorporated as a bifurcated interaction[12,13]. The ring-oxygen atom, O-4, is not included in the hydrogen bonding; its nearest intermolecular neighbor is a methylene hydrogen atom (H-2) at 2.63 Å. The geometry of the hydrogen bonds is shown in Fig. 3. The infinite chain of hydrogen bonds forms a spiral that extends around the screw axis in the *x* direction. The separation of the two carbonyl oxygen atoms across the screw axes in a dipolar arrangement is such that the O-1···O-1 distance is 3.339(1) Å.

ACKNOWLEDGMENT

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