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CONFORMATIONAL STUDIES ON ALDONOLACTONES BY N.M.R. SPECTROSCOPY. CONFORMATIONS OF D-GLUCONO-, D-MANNONO-, D-GULONO- AND D-GALACTONO-1,4-LACTONE IN SOLUTION*†

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ABSTRACT

The conformations of D-glucono-, D-mannono-, D-gulono-, and D-galactono-1,4-lactone in solution were studied by ^{1}H- and ^{13}C-n.m.r. spectroscopy. The two equilibrating, envelope forms [^3E(D) and E_3(D)] of the lactone ring are weighted strongly in favor of the conformation having the OH-2 group quasiequatorially oriented, except for D-glucono-1,4-lactone. Side-chain CHOHCH$_2$OH groups adopt orientations devoid of unfavorable, 1,3-parallel interactions of OH groups.

INTRODUCTION

The importance of aldonic and aldaric acids in metabolism is well established[2]. Some aldono- and aldaro-lactones are highly specific, competitive inhibitors of certain glycosidases[3], and information on the conformational properties of sugar lactones is important for detailed understanding of their chemical and biological behavior. The accompanying papers describe the conformations of D-glucarolactones[4] and D-pentono-1,4-lactones[5] in solution as revealed by n.m.r. spectroscopy.

Among the D-hexono-1,4-lactones, the solid-state conformations of D-galactono-1,4-lactone[6], D-gulono-1,4-lactone[7], and 2,3,6-tri-*O*-methyl-D-galactono-1,4-lactone[8] have been determined; all of these lactones adopt envelope conformations having the OH-2 group quasiequatorially oriented. Envelope conformations have been considered for some hexono-1,4-lactones in solution[9,10], but these have not been firmly established by experiment.

The present work is a ^{1}H- and ^{13}C-n.m.r. spectroscopic study of four D-hexono-1,4-lactones of biological interest, namely, D-glucono-1,4-lactone (**1**), D-mannono-1,4-lactone (**2**), D-gulono-1,4-lactone (**3**), and D-galactono-1,4-lactone (**4**).

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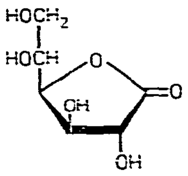

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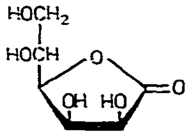

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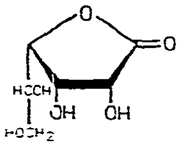

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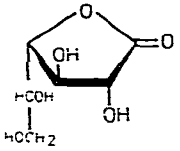

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RESULTS AND DISCUSSION

^{1}H-N.m.r. spectra. — No systematic, ^{1}H-n.m.r. studies of hexono-1,4-lactones appear to have been undertaken thus far. Although ^{1}H-n.m.r. spectra of **1** in D_2O were recorded[11] at 60 MHz, the spectra were not of first order, and no conformational information was obtained from them. Likewise, ^{1}H-n.m.r. spectra of the per-*O*-methyl derivative of **1** were recorded at 60 MHz, but only the chemical shifts of *O*-methyl groups were given[12]. Recently, ^{1}H-n.m.r. data, including some coupling constants, have been determined[12a] for partially silylated derivatives of **1**–**4**.

The ^{1}H-n.m.r. spectra of compounds **1**–**4** were recorded at 100 MHz, deuterium oxide, methanol-d_4, pyridine-d_5, and dimethyl sulfoxide-d_6 being used as the solvents. As aids to spectral resolution, a lanthanide shift-reagent or the per-*O*-acetyl derivatives were used in some instances. Computer-simulated spectra were also generated, in order to verify assigned ^{1}H-n.m.r. chemical-shifts and coupling-constants. Chemical-shift and coupling-constant data are given in Table I.

Chemical shifts. — The remarks made earlier regarding D-pentono-1,4-lactones[5] appear also to be valid for the D-hexono-1,4-lactones. The C-5 protons in the latter resonate at somewhat lower field than H-6 and H-6'.

Coupling constants. — Proton–proton coupling-constants for the D-hexono-1,4-lactones are similar to those of corresponding lactones studied earlier[4,5]; their magnitudes were indicative of conformational equilibria between two envelope forms. Coupling constants found for the side-chain protons were largely consistent with expectations based on work with acyclic sugars[13] and with data reported for D-pentononitriles[14] and D-hexononitriles[15], and D-hexonic acids[16].

^{13}C-N.m.r. spectra. — Proton-decoupled, natural-abundance-^{13}C, pulse Fourier-transform, n.m.r. spectra of **1**–**4** were recorded for solutions in D_2O before and after

TABLE I

100-MHz, ^{1}H-N.M.R. DATA FOR D-GLUCONO-1,4-LACTONE (**1**), D-MANNONO-1,4-LACTONE (**2**), D-GULONO-1,4-LACTONE (**3**), D-GALACTONO-1,4-LACTONE (**4**), AND 2,3,5,6-TETRA-*O*-ACETYL-D-GALACTONO-1,4-LACTONE

Compound	*Solvent*	*Chemical shifts in δ values*[a]						*Coupling constants in Hz*					
		H-2	*H-3*	*H-4*	*H-5*	*H-6*	*H-6′*	$^3J_{2,3}$	$^3J_{3,4}$	$^3J_{4,5}$	$^3J_{5,6}$	$^3J_{5,6'}$	$^2J_{6,6'}$
1	CD_3OD	4.27d	4.37q	4.56q	4.00o	3.78q	3.70q	4.5	5.0	6.0	3.9	5.7	−11.5
	$(CD_3)_2SO$[b]	4.52d	4.63q	4.89q	4.26o	3.98q	3.54q	3.8	4.6	6.9	3.8	5.7	−11.5
	C_5D_5N	4.89m	4.95m	5.07q	4.59o	4.23q	4.15q	4.3	4.5	6.6	4.0	5.2	−11.5
2	D_2O	5.07d	4.94q	4.78q	4.34q	4.16q	4.03q	4.5	2.6	8.9	2.8	5.1	−12.0
	CD_3OD	4.54d	4.47q	4.31q	3.97o	3.81q	3.63q	4.6	2.4	8.9	2.8	5.1	−11.7
	$(CD_3)_2SO$[b]	4.92d	4.73q	4.03q	4.21o	4.06q	3.86q	4.3	2.6	8.6	2.6	5.2	−11.6
	C_5D_5N	4.85d	4.96q	4.77q	4.65o	4.20q	3.98q	4.3	2.3	9.0	2.6	4.4	−11.5
3	D_2O	4.75d	4.58q	4.52q	4.09o	3.83q	3.71q	4.6	2.7	5.3	3.9	5.5	−12.2
	$(CD_3)_2SO$	4.91d	4.72q	4.67q	4.25o	4.00q	3.94q	4.6	2.6	4.5	3.8	5.2	−11.8
4	C_5D_5N	5.03d	5.25t	4.92q	4.52m	4.28m	4.22m	8.5	8.0	2.4	5.5	7.7	−11.0
tetraacetate	$CDCl_3$[c]	5.58d	5.37q	4.53q	5.25q	4.31q	4.15q	7.1	6.6	2.9	5.4	6.5	−11.9
	$(CD_3)_2SO$[d]	5.78d	5.47t	4.84q	5.32o	4.29q	4.20q	7.5	7.0	3.5	5.4	6.4	−11.9

[a] Signal multiplicities: d, doublet; m, complex multiplet; o, octet; q, quartet; t, triplet. [b] In the presence of CF_3CO_2H. [c] Chemical shifts of acetyl-group protons: δ 2.10, 2.08, 2.04, and 2.00. [d] Chemical shifts of acetyl-group protons: δ 2.13, 2.09, 2.07, and 2.03.

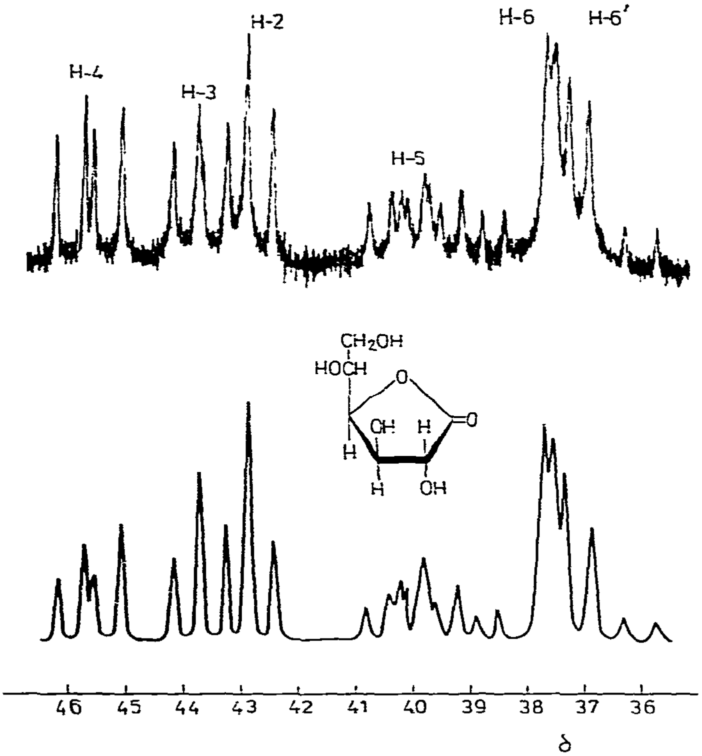


Fig. 1. The 100-MHz, ^{1}H-n.m.r. spectrum of D-glucono-1,4-lactone (**1**) in methanol-d_4 (upper trace) and the simulated spectrum (lower trace).

mutarotation, and in dimethyl sulfoxide-d_6. Assignments were made by following assumptions described earlier[4,5]. Chemical shifts and "solvent-induced" shifts[5] are given in Tables II and III. The resonances of C-1, C-2, C-3, and C-4 of D-hexono-1,4-lactones appear at fields similar to those characteristic of C-1, C-2, C-3, and C-4 of D-pentono-1,4-lactones[5] having the same ring-carbon configurations. The C-5 resonances for D-hexono-1,4-lactones are shifted to lower field (71.3–68.7 p.p.m. in D_2O), as the secondary C-5 atoms in D-hexono-1,4-lactones are deshielded in comparison with the (primary) C-5 atoms in D-pentono-1,4-lactones. Comparison of the data for the D-pentono-1,4-lactones and the D-hexono-1,4-lactones showed that C-2 and C-3, and also C-1, C-4, and C-5, experience similar shielding and deshielding effects. The relative positions of corresponding carbon-resonances in D-hexono-1,4-lactones and D-hexonic acids[16] are similar to those observed for D-pentono-1,4-lactones and D-pentonic acids[5]. The C-6 resonances for D-hexono-1,4-lactones appear at slightly higher field, δ 62.5–63.5 p.p.m. in D_2O, than those for D-hexonic acids[16].

All resonances are shifted to higher field in dimethyl sulfoxide-d_6 in comparison with solutions in D_2O, but not to the same extent. Regularities similar to those found for D-pentono-1,4-lactones and D-pentonic acids[5] were observed.

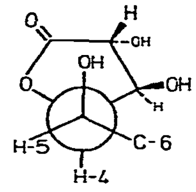
TABLE II

CARBON-13 CHEMICAL-SHIFTS FOR SOME D-HEXONO-1,4-LACTONES IN D_2O AT ~30°

Compound	*Chemical shifts in p.p.m. downfield from Me_4Si*[a]					
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
D-Glucono-1,4-lactone (**1**)	177.8	74.0[b]	73.55[b]	80.65	71.3	63.35
D-Mannono-1,4-lactone (**2**)	178.9	71.6[b]	70.4[b]	79.55	68.65	63.5
D-Gulono-1,4-lactone (**3**)	178.9	71.8[b]	71.1[b]	82.3	70.6	62.55
D-Galactono-1,4-lactone (**4**)	176.9	74.6[b]	73.8[b]	81.1	69.9	63.0

[a] Original data, referenced to the highest-field resonance of DSS, were converted according to the empirical equation[4,5]: δ Me_4Si = δ DSS − 1.6. Assignments were made following principles established for 1,4-lactones and for furanoid sugars, as described earlier[4,5]. Comparisons of the hexono-1,4-lactones and the hexonic acids[16] with each other and with other, related compounds[4,5] were made. [b] Assignments may have to be reversed.

Conformational features of individual D-*hexono-1,4-lactones.* — D-*Glucono-1,4-lactone* (**1**). Coupling constants found for **1** (see Table I and Fig. 1) indicate that the ^{3}E(D) $\rightleftarrows$ E_3(D) equilibrium exists in solution, with the ^{3}E(D), *tg*, *g′t′* conformational state being favored (see Table IV). The ^{3}E(D) conformation, having HO-2 quasiaxial, was somewhat unexpected, but is clearly indicated from the ^{1}H-n.m.r. data. Chiroptical properties[12a,18] of **1** have been interpreted as favoring the E_3(D) conformation of the lactone ring in **1**, but this assignment may require revision, as the molecular ellipticities observed may be the sum of two effects, one of configuration at C-2, the other of ring geometry[19].



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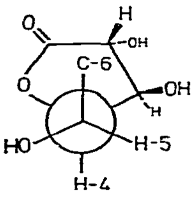

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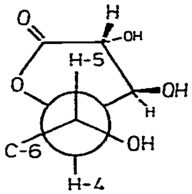

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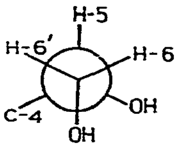

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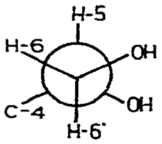
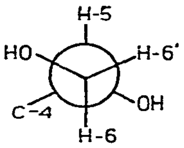


1-*g′t′*



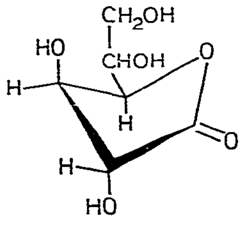
1-*t′g′*

TABLE III

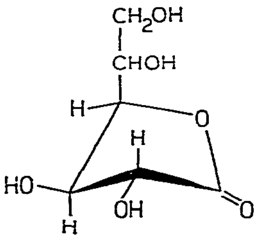
CARBON-13 CHEMICAL-SHIFTS OF SOME D-HEXONO-1,4-LACTONES IN Me_2SO-d_6

Compound	*Chemical shifts in p.p.m. downfield from internal Me_4Si, and solvent-induced shifts $\Delta\delta$*[a] *(in parentheses)*					
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
D-Glucono-1,4-lactone (**1**)	175.5(2.3)	73.1[b](0.9)	72.7[b](0.85)	79.9(0.75)	69.4(1.9)	62.7(0.6)
D-Mannono-1,4-lactone (**2**)	176.2(2.7)	70.6[b](1.0)	69.1[b](0.5)	78.0(1.55)	67.8(0.85)	62.8(0.7)
D-Gulono-1,4-lactone (**3**)	175.9(3.0)	70.4[b](1.4)	69.9[b](1.2)	80.5(1.8)	69.3(1.3)	61.7(0.85)
D-Galactono-1,4-lactone (**4**)	174.6(2.3)	73.7[b](0.9)	72.5[b](1.3)	79.4(1.7)	68.2(1.7)	61.7(1.3)

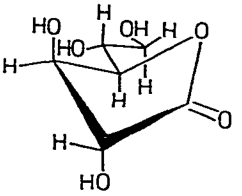
[a] $\Delta\delta = \delta D_2O - \delta Me_2SO$-$d_6$. [b] Assignments may have to be reversed.



1-³*E* (D)



1 – *E*₃(D)



1- ³*E* (D) . *tg* . *g′t′*

Interestingly, in D-glucaro-1,4-lactone, a corresponding conformational equilibrium was found to be shifted toward the E_3(D) conformation, which has OH-2 quasiequatorially oriented, and OH-5 is situated over the lactone ring[4]; it seems probable that the CO_2H group in the aldarolactone makes intramolecular hydrogen-bonding and stabilization easier than in **1**. Furthermore, the CO_2H group in the

TABLE IV

CONFORMER POPULATIONS FOR D-GLUCONO-1,4-LACTONE (**1**), D-MANNONO-1,4-LACTONE (**2**), D-GULONO-1,4-LACTONE (**3**), AND D-GALACTONO-1,4-LACTONE (**4**) AND ITS 2,3,5,6-TETRA-*O*-ACETYL DERIVATIVE, IN SOLUTION

Compound	*Solvent*	*Lactone-ring conformational contributions in percent*[a]		*Exocyclic CHOHCH$_2$OH group conformational contributions in percent*[b,c]				
		³E	E3			g′g′	*g′t′ (t′g′)*	*t′g′ (g′t′)*
				gg + gt	*tg*			
1	CD_3OD	70	30	50	50	35	40	25
	$(CD_3)_2SO$	80	20	45	55	35	40	25
	C_5D_5N	80	20	50	50	40	50	10
2	D_2O	100	0	25	75	50	35	15
	CD_3OD	100	0	25	75	50	35	15
	$(CD_3)_2SO$	100	0	30	70	50	40	10
	C_5D_5N	100	0	25	75	50	35	15
				gg + tg	*gt*			
3	D_2O	0	100	50	40	35	25	40
	$(CD_3)_2SO$	0	100	70	30	40	25	35
4	C_5D_5N	15	85	90	10	0	40	60
tetraacetate	$CDCl_3$	30	70	85	15	10	40	50
	$(CD_3)_2SO$	25	75	80	20	10	35	55

[a] Calculated for **1** from the coupling constants between the cisoidal H-3 and H-4, as for D-xylono-1,4-lactone[5], for **2** as for D-lyxono-1,4-lactone[5], for **3** as for D-lyxono-1,4-lactone[5], and for **4** and its tetraacetate as for D-arabinono-1,4-lactone[5]. [b] Calculated from the Karplus relation with $J_{60°} = 1.5$ and $J_{180°} = 11.5$ Hz, as for nucleosides[17]. [c] See corresponding formulas for the assignment of H-6 and H-6′; the assignments are, to some extent, arbitrary, and may have to be reversed.

TABLE V

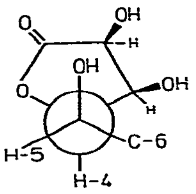
100-MHz, ^{1}H-N.M.R. DATA FOR D-GLUCONO-1,4-LACTONE (1) IN METHANOL-d_4 IN THE PRESENCE OF PrCl$_3$ AT ~30°

Equiv. of PrCl$_3$ added	*Chemical shifts in δ values*[a] *and lanthanide-induced shifts*[b] *in Δδ (in parentheses)*						*Coupling constants in Hz*					
	H-2	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	$^3J_{2,3}$	$^3J_{3,4}$	$^3J_{4,5}$	$^3J_{5,6}$	$^3J_{5,6'}$	$^2J_{6,6'}$
0.0	4.27d	4.37q	4.56q	4.00o	3.78q	3.70q	4.5	5.0	6.6	3.9	5.7	−11.5
0.2	4.25d (−0.02)	4.36q (−0.01)	4.56q (0.00)	4.01o (0.01)	3.81q (0.03)	3.72q (0.02)	4.5	5.0	6.7	3.7	5.7	−11.6
0.4	4.25d (−0.02)	4.36q (−0.01)	4.56q (0.00)	4.04o (0.04)	3.84q (0.06)	3.75q (0.05)	4.5	5.0	6.6	3.8	5.6	−11.7
0.6	4.24d (−0.03)	4.35q (−0.02)	4.56q (0.00)	4.05o (0.05)	3.87q (0.09)	3.78q (0.08)	4.5	5.0	6.5	3.8	5.7	−11.5

[a] Signal multiplicities as in Table I. [b] Upfield shifts negative.

aldarolactone undoubtedly influences the conformational equilibrium in solution through changes in local dipole-moments of the molecule.

It should also be noted that addition of $PrCl_3$ does not affect the coupling constants and only slightly affects the chemical shifts (see Table V), whereas such addition strongly affects chemical shifts[4] of D-glucaro-1,4-lactone. Amounts of $PrCl_3$ approximately 10 times those used with D-glucaro-1,4-lactone are needed in order to produce observable changes in chemical shifts for **1**, possibly because of the absence of a CO_2H group in **1**. Aldonic acids have been reported to chelate a lanthanide cation through the α-carboxy, α-hydroxy, and β-hydroxy oxygen atoms[20]. The origin of interactions between polyols and Pr^{3+}, Eu^{3+}, and Nd^{3+} has been discussed in detail[21]. An interesting feature of the ^{13}C-n.m.r. spectra of **1** is some deshielding of C-5, especially in D_2O, in comparison with other hexono-1,4-lactones studied, together with slight shielding of C-2 and slight deshielding of C-5, in comparison with D-glucaro-1,4-lactone[4]; all of the foregoing effects accord with a favored ^3E(D) conformation of **1**.



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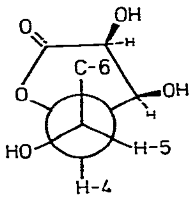

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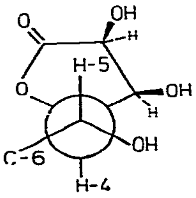

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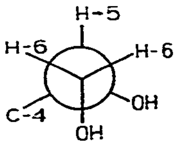
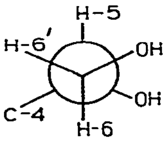
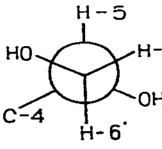


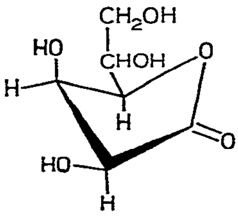
2-*g'g'*



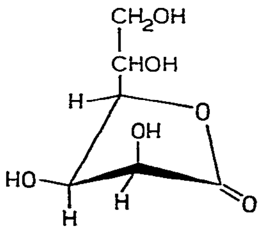
2-*g't'*



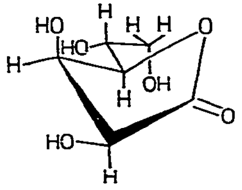
2-*t'g'*



2-^3E(D)

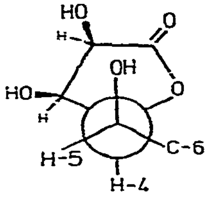


2-E_3(D)

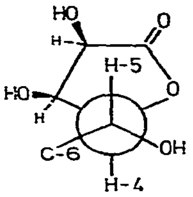


2-^3E(D), *tg*, *g'g'*

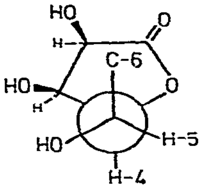
D-*Mannono-1,4-lactone* (**2**). Coupling constants observed for **2** (see Table I) are consistent with a conformational equilibrium in solution (see Table IV) between the aforedepicted conformations. The equilibrium appears to be shifted far in favor of the ^3E(D)*tg,g'g'* conformation; the relatively large shielding of C-4 and C-5 provides additional evidence for this conclusion. Contribution from the E_3(D) form is negligible.



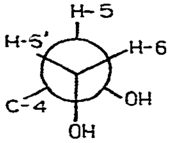
3-*gg*



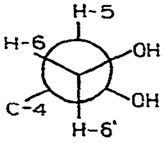
3-*gt*



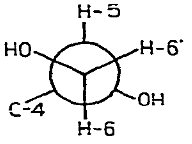
3-*tg*



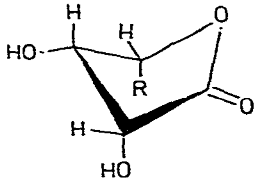
3-*g'g'*



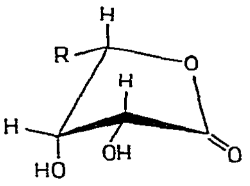
3-*g't'*



3-*t'g'*

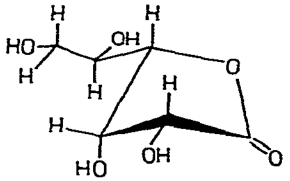


3-^3E(D)



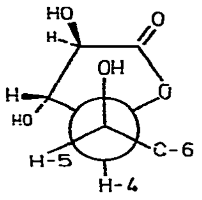
3-E_3(D)

R= $CHOHCH_2OH$

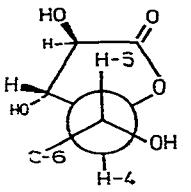


3-E_3(D), *gt, g't'*

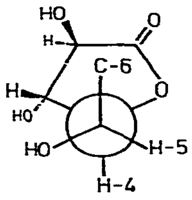
D-*Gulono-1,4-lactone* (**3**). For this lactone in solution, the coupling data (see Table I) indicate essentially exclusive population of the E_3(D) conformer (see Table IV). The E_3(D), *gt,g'g'* conformation has been found for **3** in the crystalline state[7]. Ring-carbon resonances in the ^{13}C-n.m.r. spectra of **3** appear at fields similar to those found for corresponding carbon atoms of L-gularo-1,4-lactone (D-glucaro-6,3-lactone)[4] and D-lyxono-1,4-lactone[5], both of which have similar geometry in the lactone ring. The avoidance of an unfavorable interaction between HO-3 and HO-5 constitutes a major factor in determining the favored conformational state of **3**.



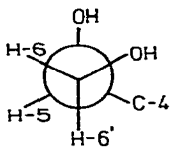
4-*gg*



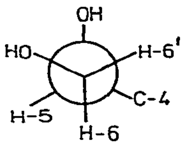
4-*gt*



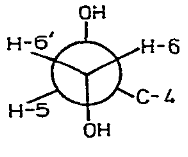
4-*tg*



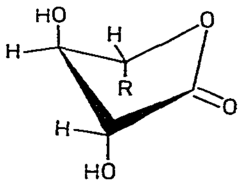
4-*g′g′*



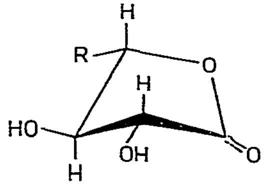
4-*g′t′*



4-*t′g′*

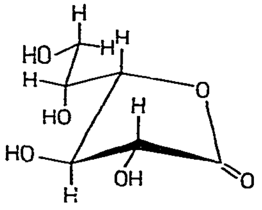


4-^{3}E(D)



4-E_3(D)

R=CHOHCH$_2$OH



4-E_3(D), *gg*, *g′t′*

D-*Galactono-1,4-lactone* (**4**). For compound **4** in solution, the coupling constants (see Table I and Fig. 2) are consistent with a conformational equilibrium between the aforedepicted conformations strongly shifted (see Table IV) toward the E_3(D) conformation. The E_3(D),*gg*,*g′t′* conformation was found for **4** in the crystalline state[6]. Resonances of the lactone-ring carbon atoms appear at very similar fields in the ^{13}C-n.m.r. spectra of **4** and D-arabinono-1,4-lactone[5], which have the same geometry of the lactone ring.

General conclusions on conformations of D-*hexono-1,4-lactones in solution.* — Conformational equilibria between two envelope forms [^{3}E(D) and E_3(D)] are generally weighted toward the conformation having OH-2 quasiequatorially oriented. Similar tendencies have been found for D-pentono-1,4-lactones[5] and partially silylated derivatives[12a] of **1**–**4** in solution, and for D-hexono-1,4-lactones in the crystalline state[6–8]. The side chain (CHOHCH$_2$OH) on C-4 in D-hexono-1,4-lactones generally favors an orientation in which 1,3-parallel interactions[13] of OH groups are avoided.

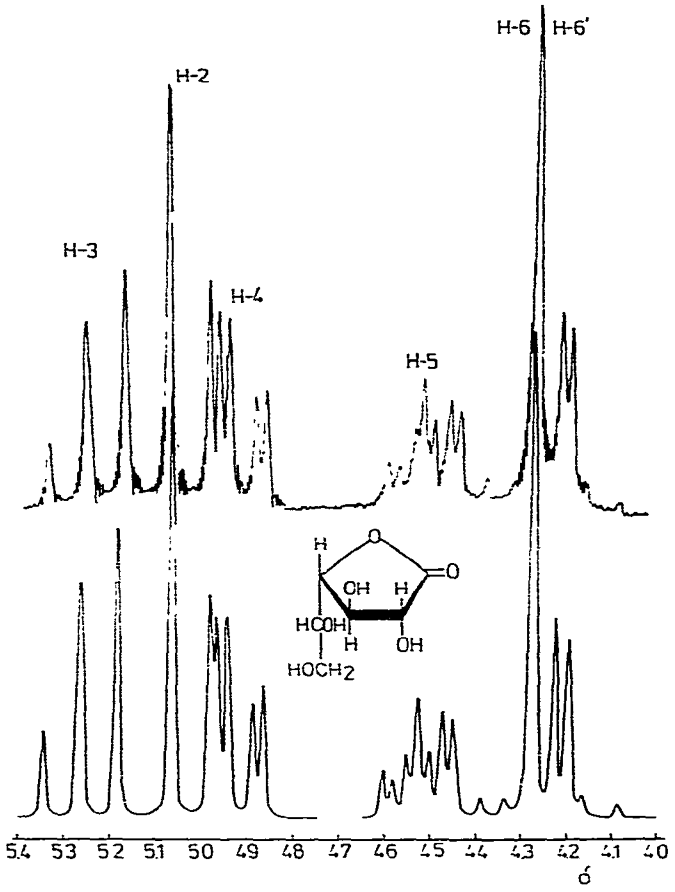


Fig. 2. The 100-MHz, ^{1}H-n.m.r. spectrum of D-galactono-1,4-lactone (4) in pyridine-d_5 (upper trace), and the simulated spectrum (lower trace).

In D-glucono-1,4-lactone (**1**), the orientation of the C-4 side-chain appears to dictate the ^3E(D) conformation of the lactone ring, in which OH-2 is quasiaxially oriented. Changes of the solvent does not exert any significant effect on the conformational equilibria (see Table IV). In contrast, peracetylation influences the equilibria, indicating that, as with D-pentono-1,4-lactones[5], intramolecular hydrogen-bonding takes part in the stabilization of the favored conformations.

EXPERIMENTAL

Materials. — D-Galactono-1,4-lactone and D-gulono-1,4-lactone were obtained from Pfanstiehl Labs., Waukegan, Illinois. Literature procedures were used for preparing D-glucono-1,4-lactone[22], D-mannono-1,4-lactone[22], and 2,3,5,6-tetra-*O*-acetyl-D-galactono-1,4-lactone[23]. All compounds had physical constants in agreement with published values and were chromatographically homogeneous. T.l.c. was performed as described earlier[4,5].

^{1}*H-N.m.r. spectra.* — Spectra were recorded at 100 MHz, as described earlier[4,5]. Spectra were computer-simulated with the aid of the program LAOCOON III.

^{13}*C-N.m.r. spectra.* — Proton-decoupled, natural-abundance-carbon-13, pulse, Fourier-transform, n.m.r. spectra were recorded as described earlier[4,5].

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