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Short Communication

The Crystal and Molecular Structures of Five-Carbon and Six-Carbon Isosaccharino-1,4-lactones from Alkaline Pulping

Raimo Alén and Jussi Valkonen†

Department of Chemistry, University of Jyväskylä, PO Box 35, FIN-40351 Jyväskylä, Finland

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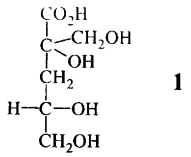
Especially in kraft pulping, the pulp industry generates enormous quantities of hydroxymonocarboxylic acids as waste from wood polysaccharides.[1] One of the main base-catalysed degradation products of cellulose and glucomannans is 3-deoxy-2-hydroxymethyl-D-pentonic acid (glucoisosaccharinic acid) (**1**), whereas the degradation of wood xylan readily results in the formation of 3-deoxy-2-*C*-hydroxymethyltetronic acid (xyloisosaccharinic acid (**2**). In conjunction with our studies on the utilization of these acids, the crystal structures of the corresponding 3-deoxy-2-*C*-hydroxymethyl-D-*erythro*-pentono-1,4-lactone (**3**) (GISAL) and 3-deoxy-2-*C*-hydroxymethyl-D,L-tetrono-1,4-lactone (**4**) (XISAL) were solved.



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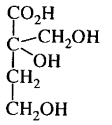

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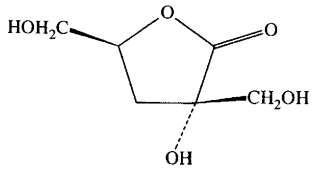

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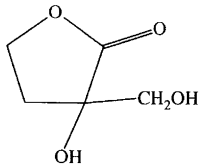

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Experimental and results

3-Deoxy-2-*C*-hydroxymethyl-D-*erythro*-pentono-1,4-lactone or α-glucoisosaccharino-1,4-lactone (**3**) was prepared by treating lactose hydrate (200 g) with aqueous calcium hydrate (54 g), isolating the calcium salt of the corresponding acid (23 g) and from that obtaining the 1,4-lactone (9 g).[2] M.p. 94.0–95.0 °C, $[\alpha]_D^{22} = +62.8°$ (*c* 1.0).

The racemic 3-deoxy-2-*C*-hydroxymethyl-D,L-tetrono-1,4-lactone or D,L-xyloisosaccharino-1,4-lactone (**4**) was isolated by vacuum distillation after lignin and cation removal from a laboratory-scale sodium hydroxide heating of birch wood.[3,4] It was recrystallised twice from ethyl acetate. M.p. 95.5–96.5 °C, $[\alpha]_D^{22} = 0°$ (*c* 1.0). This product contained 1.2% impurities as estimated from the peak areas in a gas chromatogram of its per(trimethylsilylated) derivative.

α-Glucoisosaccharino-1,4-lactone was gas-chromatographically pure.

Single-crystal data were collected with an Enraf Nonius CAD4 single-crystal diffractometer. Crystals were mounted on the top of a glass fibre and were measured at room temperature in an air atmosphere. Unit-cell dimensions were calculated using least-squares refinement of 25 randomly searched reflections. The diffractometer was controlled using the program CAD4.[5] More information is listed in Table 1. During data collection standard reflections were measured every 60 min. There was no loss of intensity in GISAL, but intensities of XISAL

† To whom correspondence should be addressed.

Table 1. Crystal data.

Compound	XISAL	GISAL
Chemical formula	$C_5H_8O_4$	$C_6H_{10}O_5$
Formula weight	132.12	162.14
Colour	White	White
No. of reflections in unit-cell determination	25	25
θ range in unit-cell determination/°	5.2–12.0	4.6–13.4
Crystal size/mm	0.1, 0.1, 0.3	0.1, 0.2, 0.2
a/Å	6.744(2)	6.184(2)
b/Å	8.560(2)	8.932(1)
c/Å	10.305(4)	6.566(1)
β/°	99.10(3)	94.09(2)
V/Å^3	587.4(3)	361.8(2)
Z	4	2
D_{calc}/Mg m^{-3}	1.49	1.49
System	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
F(000)	280	172
λ(Mo K_α)/Å	0.71073	0.71073
μ(Mo K_α)/cm^{-1}	1.23	1.23
θ range in data collection/°	2.0–25.0	2.3–30.0
Scan speed (in ω)/°min^{-1}	0.8–5.5	0.7–8.3
Data collection mode	ω/2θ	ω/2θ
h_{min}, h_{max}	0, +8	0, +8
k_{min}, k_{max}	0, +10	0, +12
l_{min}, l_{max}	−12, +12	−9, +9
No. of collected data	1104	1123
No. of unique data	1104	1123
Criterion for observed data	$I > 3\sigma(I)$	$I > 3\sigma(I)$
No. of observed data	377	701
Max. and min. absorption (DIFABS[7])	1.23/0.80	1.09/0.77
R	0.036	0.030
R_w	0.040	0.030
S	0.866	0.296
No. of refined parameters	114	139

were corrected for 5% decay. Lorentz and polarisation corrections were applied to the data, scattering factors were taken from Ref. 6 (Tables 2.2B and 2.3.1), and an absorption correction was made using the program DIFABS.[7] Data reduction and refinement were calculated using the program package MolEN,[8] structures were solved with MULTAN[9] and pictures were generated with ORTEP.[10] Nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Hydrogen atoms were found from an electron density map. Refinement was based on structure factors and unit weights. Stereo-

Table 2. Fractional coordinates and their estimated standard deviations for XISAL.

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
O1	0.3935(5)	0.1907(5)	0.0460(3)	0.035(2)
O2	0.1576(5)	0.3720(5)	0.0445(4)	0.040(2)
O3	0.4964(5)	0.5617(4)	0.1649(4)	0.033(2)
O4	0.3613(5)	0.2248(5)	0.3474(4)	0.041(2)
C1	0.3233(8)	0.3229(7)	0.0858(5)	0.031(3)
C2	0.4747(7)	0.4011(6)	0.1908(5)	0.022(2)
C3	0.6671(8)	0.3148(7)	0.1810(5)	0.034(3)
C4	0.6009(9)	0.1629(8)	0.1121(6)	0.046(4)
C5	0.4023(8)	0.3818(7)	0.3224(5)	0.033(3)
H1	0.399(7)	0.601(6)	0.155(5)	0.06(2)
H2	0.430(5)	0.196(4)	0.378(3)	0.01(1)
H31	0.725(5)	0.354(4)	0.120(3)	0.00(1)
H32	0.749(9)	0.293(8)	0.260(6)	0.08(2)
H41	0.593(6)	0.082(5)	0.163(4)	0.03(1)
H42	0.674(12)	0.125(12)	0.025(8)	0.05(4)
H51	0.491(6)	0.433(5)	0.386(4)	0.02(1)
H52	0.266(8)	0.462(7)	0.322(5)	0.08(2)

Table 3. Fractional coordinates and their estimated standard deviations for GISAL.

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
O1	0.2086(3)	0.1000	0.0084(3)	0.030(1)
O2	0.5331(3)	0.0676(3)	0.1736(3)	0.041(1)
O3	0.1779(3)	0.0683(3)	0.4798(3)	0.031(1)
O4	0.4765(4)	0.4062(3)	0.3427(4)	0.038(1)
O5	−0.1636(3)	0.1267(3)	−0.2909(3)	0.032(1)
C1	0.3503(4)	0.1137(4)	0.1718(4)	0.029(1)
C2	0.2409(4)	0.1869(3)	0.3490(4)	0.024(1)
C3	0.0351(4)	0.2518(3)	0.2418(4)	0.026(1)
C4	−0.0072(4)	0.1513(3)	0.0575(4)	0.025(1)
C5	0.3871(5)	0.2962(4)	0.4705(5)	0.033(1)
C6	−0.1160(5)	0.2270(4)	−0.1273(4)	0.029(1)
H1	0.276(5)	0.028(4)	0.532(5)	0.05(1)
H2	0.400(6)	0.454(4)	0.330(6)	0.06(1)
H3	−0.075(4)	0.118(4)	−0.353(4)	0.03(1)
H31	0.064(5)	0.347(4)	0.199(5)	0.04(1)
H32	−0.074(5)	0.259(4)	0.342(5)	0.04(1)
H41	−0.082(4)	0.066(3)	0.094(4)	0.02(1)
H51	0.298(5)	0.343(4)	0.581(5)	0.04(1)
H52	0.511(6)	0.245(4)	0.537(5)	0.05(1)
H61	−0.017(5)	0.309(4)	−0.165(5)	0.04(1)
H62	−0.252(4)	0.272(4)	−0.086(5)	0.03(1)

Table 4. Interatomic bond distances (in Å) and their estimated standard deviations.

Bond	XISAL	GISAL
C1–O1	1.317(7)	1.342(3)
C1–O2	1.207(6)	1.202(3)
C1–C2	1.521(7)	1.533(4)
C2–O3	1.412(6)	1.435(4)
C2–C3	1.510(8)	1.524(4)
C2–C5	1.522(7)	1.518(4)
C3–C4	1.514(9)	1.514(4)
C3–H31	0.86(4)	0.92(4)
C3–H32	0.92(6)	0.98(3)
C4–O1	1.476(7)	1.468(3)
C4–H41	0.88(4)	0.93(3)
C4–H42/C6	1.14(9)	1.505(4)
C5–O4	1.404(7)	1.429(4)
C5–H51	0.93(4)	1.03(3)
C5–H52	1.15(6)	0.97(3)
C6–O5		1.414(4)
C6–H61		0.99(3)
C6–H62		0.99(3)
O3–H1	0.73(5)	0.76(3)
O4–H2	0.57(3)	0.64(4)
O5–H3		0.71(3)

isomerism (absolute configuration at C2) of GISAL was not determined, but was taken from α-glucoisosaccharinic acid as determined in the literature.[11–13] The absolute configuration at C4 was known because α-glucoiso-

Table 5. Interatomic bond angles (in °) and their estimated standard deviations.

Angle	XISAL	GISAL
O1–C1–O2	123.2(5)	122.5(3)
O1–C1–C2	111.5(4)	110.3(2)
O2–C1–C2	125.3(5)	127.2(2)
O3–C2–C1	111.9(4)	107.0(2)
O3–C2–C3	110.4(4)	107.7(2)
O3–C2–C5	109.4(4)	109.7(2)
C1–C2–C3	103.0(4)	102.2(2)
C1–C2–C5	108.2(4)	113.2(2)
C3–C2–C5	114.0(4)	116.4(2)
C2–C3–C4	105.0(4)	103.6(2)
O1–C4–C3	105.4(5)	104.6(2)
O1–C4–C6		108.9(2)
C3–C4–C6		114.8(2)
O4–C5–C2	111.6(5)	112.0(2)
O5–C6–C4		112.6(2)
C1–O1–C4	110.8(4)	110.4(2)

Table 6. Hydrogen bond distances (in Å) and their estimated standard deviations. All bonds are intermolecular.

O_a–H	H···O_b	O_a–H···O_b	O_a	H	O_b	Compund
0.73(5)	2.05(5)	172(4)	O3	H1	O4	XISAL
0.76(3)	2.01(3)	176(4)	O3	H1	O4	GISAL
0.57(3)	2.19(3)	162(4)	O4	H2	O2	XISAL
0.64(4)	2.13(4)	176(4)	O4	H2	O5	GISAL
o.71(3)	2.02(3)	173(4)	O5	H3	O3	GISAL

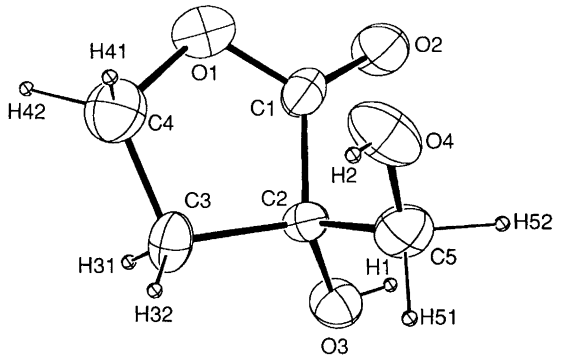

Fig. 1. The molecule of 3-deoxy-2-*C*-hydroxymethyl-D,L-tetrono-1,4-lactone (XISAL).

saccharinic acid originates from monosaccharide moieties belonging to the D-series.[14] All calculations were carried out with a MicroVAX 3100 computer.

Crystal data are listed in Table 1, fractional coordinates in Tables 2 and 3, interatomic distances in Table 4, interatomic bond angles in Table 5 and hydrogen bonds in Table 6. Molecules are drawn in Figs. 1 and 2, and unit-cell contents in Figs. 3 and 4.

The structures of the two compounds are equal except for the $-CH_2OH$ group at C4 in GISAL. In both molecules the C1–O1 bond is short [1.317(7), 1.342(3)] relative to a normal C–O single bond. This is so because O2 is double-bonded to C1. The situation is similar in ambluodiol (formula $C_{17}H_{22}O_7$),[15] florigrandin (formula $C_{20}H_{30}O_7$)[16] and solstitalin (formula $C_{15}H_{20}O_5$),[17] which are the only compounds in the Cambridge Structural Database that have a structure of the xyloisosaccharino-

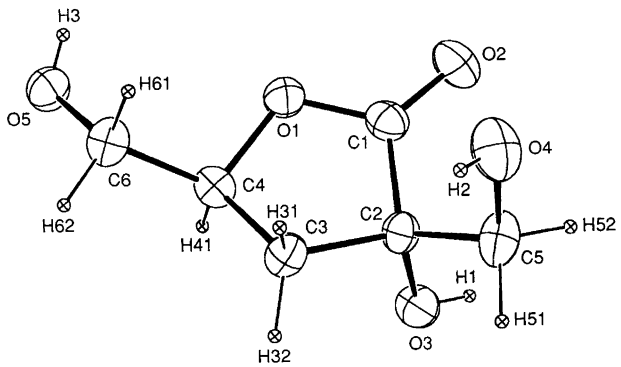

Fig. 2. The molecule of 3-deoxy-2-*C*-hydroxymethyl-D-*erythro*-pentono-1,4-lactone (GISAL).

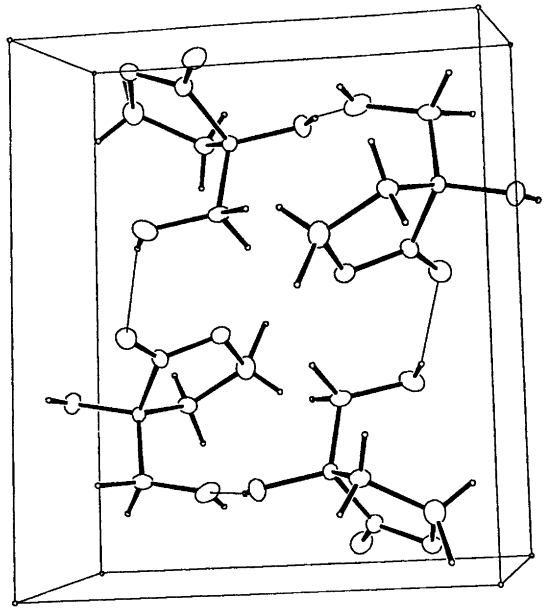

Fig. 3. The unit-cell content of 3-deoxy-2-*C*-hydroxymethyl-D,L-tetrono-1,4-lactone (XISAL). The ***b***-axis is horizontal and ***c***-axis vertical. Single lines indicate hydrogen bonds.

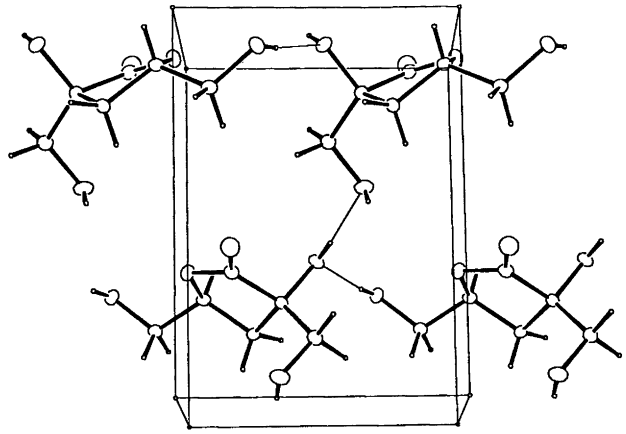

Fig. 4. The unit-cell content of 3-deoxy-2-*C*-hydroxymethyl-D-*erythro*-pentono-1,4-lactone (GISAL). The ***c***-axis is horizontal and ***b***-axis vertical. Single lines indicate hydrogen bonds.

1,4-lactone type. All the other bonds and bond angles are normal when compared with the literature values.

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