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The Crystal and Molecular Structure of 2,2′;5,6-Di-*O*-isopropylidene-2-*C*-hydroxymethyl-L-gulonolactone

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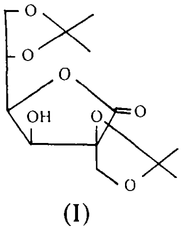
2,2′;5,6-Di-*O*-isopropylidene-2-*C*-hydroxymethyl-L-gulonolactone is monoclinic, space group $P2_1$, with a = 13·273 (13), b = 18·395 (21), c = 6·065 (6) Å, β = 100·42°, Z = 4. Refinement of the Mo $K\alpha$ diffractometer data by full-matrix least squares gave R = 0·059 for 1985 independent observed reflexions. The asymmetric unit contains two chemically identical molecules, $C_{13}H_{20}O_7$. Crystallographically significant differences exist between these two molecules. Hydrogen-bonding between crystallographically equivalent molecules links molecules along **c**.

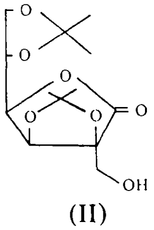
Introduction

The synthesis of optically active pheromones requires precursors of known chirality and during the investigation of possible starting materials we investigated the cyanohydrin synthesis on L-sorbose. Although the reaction of D-fructose with cyanide has been investigated (Kiliani, 1886), we could find no report of L-sorbose. This was all the more interesting in that, although D-fructose gives a mixture of isomers (Kiliani, 1928), L-sorbose appeared to produce only one product. The desired derivative was a partially blocked sugar lactone and, since the intermediate cyanohydrin and lactone showed no proclivity to crystallize, the isopropylidene derivative was prepared directly.

Diisopropylidene formation (Brimacombe & Tucker, 1966) occurred readily, as indicated by thin-layer chromatography, nuclear magnetic resonance, and mass spectrometry, to form nicely crystalline material m.p. 167·5–168 °C. To establish the configuration of the branched centre as well as the positions of the isopropylidenes, single-crystal X-ray analysis of this material was undertaken, and it is shown to be 2,2′;5,6-di-*O*-isopropylidene-2-*C*-hydroxymethyl-L-gulonolactone (I).



(I)



(II)

Subsequent preparations have provided a second isomeric diisopropylidene (II) m.p. 132–133 °C as the sole product. Attempts to recrystallize (I) or reprepare (I) have led only to (II). On the basis of this isomerization and from spectral evidence on (II) and several of its derivatives we assign to (II) the structure 2,3;5,6-diisopropylidene-2-*C*-hydroxymethyl-L-gulonolactone.

Because of their feathery nature, crystals of (II) do not lend themselves to single-crystal structure analysis.

Experimental

Crystals of the title compound were obtained as colourless plates. With a crystal mounted along **b**, precession photographs of the *hk*0 and 0*kl* zones were taken, as well as Weissenberg photographs of the *h*0*l* and *h*1*l* layers. Systematic absences for $k = 2n + 1$ were found for the 0*k*0 zone, which, with the chemical information, indicated the space group $P2_1$. Accurate cell parameters were determined by least squares from 12 strong reflexions of $2\theta > 20°$ centred on the Mo $K\alpha_1$ peak.

Crystal data

$C_{13}H_{20}O_7$, M_r = 288·29, monoclinic, $P2_1$, a = 13·273 (13), b = 18·395 (21), c = 6·065 (6) Å, β = 100·42°, V = 1456·39 Å^3, D_m = 1·23 (by measurement of crystal dimensions and weight), D_c = 1·32 g cm^{-3}, Z = 4, μ = 1·15 cm^{-1}, $F(000)$ = 616, λ(Mo $K\alpha_1$) = 0·70926 Å.

A computer-controlled (Picker) diffractometer with a scintillation counter was used to collect intensities. A θ–2θ scan was employed at a rate of 2° min^{-1} in 2θ. The base scan width was 0·9° (increased for dispersion) and background counts were carried out at each scan limit for 10 s. The maximum 2θ value was 45°. 1985 unique reflexions were obtained of which 1657 were classed as observed [$I > 2·35\sigma(I)$, $\sigma(I) = [(T) + (ts/tb)^2(B_1 + B_2) + (KI)^2]^{1/2}$ where T = total count, *ts*

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= scan time, tb = total background count time, B_1 and B_2 are the background counts, K is a constant equal to 0·03, and I is the net count}. Two standard reflexions were measured every 70 reflexions and no systematic variation was observed. The data were scaled and corrected for Lorentz and polarization effects.

Structure determination and refinement

Initial attempts to solve the structure by Patterson and tangent refinement techniques failed. Access to *MULTAN* (Germain, Main & Woolfson, 1971) then became available. From a set of 32 possible solutions one was found which led to an acceptable model. The only feature indicating the 'correct' set was ψ_0, ranked first. The absolute figure of merit, the residual, and the combined figure of merit were 31, 14 and 8 respectively. Subsequent Fourier maps led to the identification of all 40 non-hydrogen atoms in the asymmetric unit. This model was refined by full-matrix least-squares methods. H atoms were either located from difference maps or placed in calculated positions. In the final stages, the positional parameters of the H atoms were varied. Because of program limitations, one molecule was refined at a time (with only 17 H atoms allowed to move). This procedure led to a final R of 0·059 ($R = \Sigma\,|F_o| - |F_c|/\Sigma\,|F_o|$). During early stages unit weights were used but these were later replaced by weights derived from counter statistics $(1/\sigma_F)^2$. The temperature factors for the H atoms were fixed ($B = 5{\cdot}0$ Å^2) throughout.

Table 1. *Atomic coordinates*

Fractional atomic coordinates are given with estimated standard deviations in parentheses. Values for non-hydrogen atoms are $\times 10^4$; those for hydrogen atoms are $\times 10^3$

	Molecule *A*			Molecule *B*		
	x	*y*	*z*	*x*	*y*	*z*
C(1)	4851 (6)	1201 (8)	8455 (13)	3363 (6)	3806 (8)	21 (4)
O(1)	4390 (4)	1472 (7)	9751 (9)	2845 (4)	4078 (7)	1190 (9)
C(2)	4415 (6)	866 (8)	6168 (13)	3009 (6)	3399 (8)	−2164 (12)
O(2)	3542 (4)	1245 (7)	5160 (8)	2163 (4)	3757 (7)	−3504 (9)
C(2)′	4055 (6)	95 (8)	6411 (16)	2602 (7)	2654 (8)	−1740 (17)
O(2)′	3247 (4)	43 (7)	4513 (10)	1553 (5)	2726 (7)	−2250 (13)
C(3)	5335 (5)	944 (8)	4988 (12)	3964 (6)	3412 (8)	−3237 (14)
O(3)	5410 (4)	1641 (7)	4178 (8)	4059 (4)	4070 (7)	−4332 (9)
C(4)	6226 (5)	821 (8)	6909 (12)	4810 (6)	3363 (8)	−1191 (13)
O(4)	5870 (4)	1138 (7)	8870 (8)	4373 (4)	3756 (7)	576 (8)
C(5)	7220 (6)	1140 (8)	6698 (14)	5799 (6)	3703 (8)	−1403 (14)
O(5)	7943 (4)	980 (7)	8661 (10)	6489 (4)	3642 (7)	732 (10)
C(6)	7705 (7)	801 (9)	4865 (18)	6336 (8)	3314 (9)	−3044 (17)
O(6)	8752 (5)	860 (8)	5714 (14)	7112 (6)	2920 (8)	−1707 (12)
C(7)	2748 (6)	722 (8)	4300 (13)	1306 (6)	3277 (8)	−3933 (15)
C(8)	8921 (6)	926 (9)	7983 (19)	7389 (6)	3280 (8)	380 (15)
C(9)	1912 (7)	769	5691 (18)	397 (7)	3636 (10)	−3360 (18)
C(10)	2336 (6)	869 (8)	1892 (14)	1205 (9)	2978 (10)	−6231 (22)
C(11)	9434 (8)	280 (10)	9138 (26)	7609 (9)	2684 (9)	2137 (19)
C(12)	9522 (9)	1585 (10)	8631 (24)	8235 (8)	3765 (10)	486 (23)
H(C2′)	460	−34	621	283	241	−291
H(C2′)′	380	4	793	278	240	−50
H(C3)	530	57	358	399	300	−386
H(O3)	517	170	266	355	413	−562
H(C4)	637	30	745	491	288	−52
H(C5)	722	168	661	575	421	−190
H(C6)	733	108	327	658	365	−349
H(C6)′	747	23	460	597	300	−410
H(C9)	220	66	706	27	406	−472
H(C9)′	147	37	496	48	386	−200
H(C9)″	170	125	561	−14	335	−383
H(C10)	288	80	125	98	348	−67
H(C10)′	214	138	162	71	269	−637
H(C10)″	182	45	162	172	277	−649
H(C11)	940	18	1053	778	290	362
H(C11)′	999	22	868	812	241	207
H(C11)″	906	−20	856	725	235	173
H(C12)	961	162	1029	842	403	187
H(C12)′	918	202	804	798	420	−45
H(C12)″	1019	157	827	887	365	0

Table 2. *Bond distances* (Å) *and angles* (°), *with estimated standard deviations in parentheses*

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
C(1)–O(1)	1·20 (1)	1·20 (1)	C(2)–C(2)′–O(2)′	100·9 (7)	104·6 (8)
C(1)–C(2)	1·53 (1)	1·52 (1)	C(2)–O(2)–C(7)	108·5 (6)	109·8 (7)
C(1)–O(4)	1·34 (1)	1·33 (1)	C(2)′–O(2)′–C(7)	106·6 (6)	108·7 (7)
C(2)–O(2)	1·39 (1)	1·42 (1)	C(2)–C(3)–O(3)	111·6 (6)	111·7 (7)
C(2)–C(2)′	1·51 (1)	1·51 (1)	C(2)–C(3)–C(4)	101·8 (6)	101·5 (6)
C(2)–C(3)	1·53 (1)	1·53 (1)	O(3)–C(3) C(4)	108·3 (6)	108·8 (7)
O(2)–C(7)	1·45 (1)	1·43 (1)	C(3)–O(3)–H(O3)	114·9 (9)	112·5 (9)
O(2)′–C(2)′	1·43 (1)	1·38 (1)	C(3)–C(4)–O(4)	103·9 (6)	103·4 (6)
O(2)′–C(7)	1·41 (1)	1·43 (1)	C(3)–C(4)–C(5)	117·4 (7)	116·2 (7)
C(3)–C(4)	1·52 (1)	1·52 (1)	O(4)–C(4)–C(5)	109·6 (6)	108·8 (7)
C(3)–O(3)	1·39 (1)	1·41 (1)	C(1)–O(4)–C(4)	110·1 (6)	111·0 (6)
C(4)–O(4)	1·48 (1)	1·49 (1)	C(4)–C(5)–O(5)	109·0 (7)	108·4 (7)
C(4)–C(5)	1·47 (1)	1·48 (1)	C(4)–C(5)–C(6)	114·0 (7)	112·9 (8)
C(5)–O(5)	1·42 (1)	1·45 (1)	O(5)–C(5)–C(6)	102·6 (7)	104·8 (7)
C(5)–C(6)	1·52 (1)	1·51 (1)	C(5)–O(5)–C(8)	106·5 (6)	108·4 (6)
C(6)–O(6)	1·40 (1)	1·40 (1)	C(5)–C(6)–O(6)	102·9 (8)	104·6 (8)
C(8)–O(5)	1·43 (1)	1·42 (1)	C(6)–O(6)–C(8)	110·6 (7)	108·7 (8)
C(8)–O(6)	1·36 (1)	1·42 (1)	O(2)–C(7)–O(2)′	104·8 (5)	103·6 (6)
C(8)–C(11)	1·55 (2)	1·56 (2)	O(2)–C(7)–C(9)	108·7 (7)	109·9 (8)
C(8)–C(12)	1·50 (2)	1·49 (2)	O(2)–C(7)–C(10)	110·3 (7)	109·6 (8)
O(1)–H(O3)	1·92	1·99	O(2)′–C(7)–C(9)	112·3 (7)	103·9 (8)
O(3)–H(O3)	0·92	0·94	O(2)′–C(7)–C(10)	109·5 (7)	112 (1)
O(1)–C(1)–C(2)	127·7 (7)	127·5 (8)	C(9)–C(7)–C(10)	111·1 (7)	116·7 (8)
O(1)–C(1)–O(4)	122·4 (7)	123·2 (8)	O(5)–C(8)–O(6)	107·7 (7)	105·3 (6)
C(2)–C(1)–O(4)	109·8 (7)	109·0 (7)	O(5)–C(8)–C(11)	106·3 (9)	107·0 (8)
C(1)–C(2)–O(2)	110·1 (6)	110·9 (7)	O(5)–C(8)–C(12)	110·0 (8)	112·1 (9)
C(1)–C(2)–C(2)′	111·3 (7)	111·2 (7)	O(6)–C(8)–C(11)	113 (1)	106·0 (8)
C(1)–C(2)–C(3)	100·6 (6)	102·4 (6)	O(6)–C(8)–C(12)	109 (1)	114·1 (9)
C(2)′–C(2)–C(3)	115·3 (7)	115·9 (8)	C(11)–C(8)–C(12)	110·9 (9)	111·7 (9)
C(2)′–C(2)–O(2)	105·0 (6)	104·3 (6)	O(1)–H(O3)–O(3)	157·5	160·0
O(2)–C(2)–C(3)	114·7 (6)	112·4 (7)			

Table 3. *Mean planes and displacements of the atoms* (Å) *from the planes*

Equations are in the form $lX + mY + nZ + p = 0$ and refer to an orthogonal system of axes (X, Y, Z) with X along **a**, Y in the *ab* plane and Z along $\mathbf{c}^*$.

	l	m	n	p	χ^2
Plane I*A* C(2), C(2)′, C(7), O(2)	0·505	−0·166	−0·847	0·843	306·26
Plane I*B* C(2), C(2)′, C(7), O(2)	0·458	−0·339	−0·822	−0·874	1·95
Plane II*A* C(1), C(2), C(4), O(4)	0·123	0·905	−0·407	−0·594	9·50
Plane II*B* C(1), C(2), C(4), O(4)	0·161	0·855	−0·494	−6·672	5·82
Plane III*A* C(6), C(8), O(5), O(6)	0·003	0·991	−0·131	−1·126	8·93
Plane III*B* C(5), C(6), C(8), O(5)	0·456	0·870	−0·189	−9·647	4·09

Plane	Atom	Displacement	Plane	Atom	Displacement
I*A*	O(2)′	0·48	II*B*	C(3)	0·55
I*B*	O(2)′	−0·41	III*A*	C(5)	0·45
II*A*	C(3)	0·57	III*B*	O(6)	−0·39

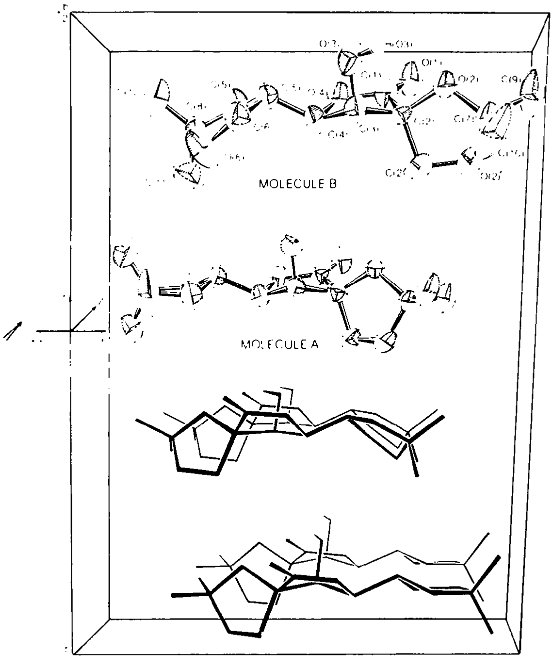

Fig. 1. A view of the unit cell illustrating the molecular packing. The upper asymmetric unit includes labels as well as 50% probability thermal ellipsoids. In order to show the hydrogen-bonding, an additional asymmetric unit has been added adjacent to the lower one. Dotted lines indicate hydrogen-bonding between H(O3) and O(3).

Programs used (other than those mentioned) were those listed by Einstein & Jones (1972). Scattering factors for C and O were from Cromer & Waber (1965), for H from Stewart, Davidson & Simpson (1965).

Table 1 contains atomic coordinates;[*] bond distances and angles are listed in Table 2. Some mean planes are reported in Table 3 with deviations of selected atoms from these planes. The packing is illustrated in Fig. 1 with the labelling of the atoms.

Discussion

Two chemically identical molecules, $C_{13}H_{20}O_7$, comprise the asymmetric unit. The structure consists of 'layers' in **b** of molecules *A*, *B* and their successive twofold screw related molecules. Each molecule is hydrogen-bonded to crystallographically identical molecules one cell edge in **c** apart. The H(O3)···O(1) lengths are 1·92 and 1·99 Å for *A* and *B* respectively.

About C(2) an *S*-configuration has been established showing the stereospecific mode of attack of the cyanide ion on the starting L-sorbopyranose. One isopropylidene is bonded across the spiro C(2) centre whereas the other links the exocyclic glycol unit C(5), O(5); C(6), O(6). Within the isopropylidene group the angle formed by planes I*B* and III*B* is 24·5°.

Bond lengths and angles within *A* and *B* are not unusual, but crystallographically significant differences between the molecules exist. Most notably the lengths C(2)′–O(2)′ in *A* and *B* are 1·43 (1) and 1·38 (1) Å and O(6)–C(8) lengths in *A* and *B* are 1·36 (1) and 1·42 (2) Å respectively. Differences in bond angles are less striking.

Each molecule contains three five-membered rings, two of which are in envelope conformations. Plane I, on the other hand, consists of C(2), C(2)′, C(7) and O(2) which form a well defined plane in molecule *B* but not in *A*. C(1), C(2), C(4) and O(4) are closely planar in both *A* and *B* with C(3) out of the plane by ~0·56 Å in both molecules. Plane III is composed of C(6), C(8), O(5) and O(6) in *A* and C(5), C(6), C(8) and O(5) in *B*. In *A*, C(5) is the non-planar atom and is displaced by 0·45 Å. The non-planar atom in *B* is O(6), deviating by 0·39 Å. Also, for both planes II and III it can be seen from Table 3 that the atoms in *B* are more planar.

Although many examples of 1,3-dioxolan ring systems have been investigated by the X-ray technique, the spiro-fused lactone structure of 2-*C*-hydroxymethyl-2,2′-*O*-cyclohexylidene-3-deoxy-5-*O*-(*p*-bromobenzenesulphonyl)-D-*erythro*-pentono-1,4-lactone (Hughes, Trotter & Howard, 1970) is the only structure analogous to the one reported here. The dissimilarity of substituents, cyclohexylidene *versus* isopropylidene, deoxy-*erythro versus* gulono, makes close comparison of these structures of questionable value.

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32569 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.