Crystal Structure of 3,6-Anhydro-α-D-glucosyl-1,4:3,6-dianhydro-β-D-fructoside

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The crystal structure of the title compound has been determined from three-dimensional data collected on a diffractometer. The structure was solved by direct methods, using phases refined by the tangent formula. The orthorhombic unit cell, space group $P2_12_12_1$ has dimensions: $a = 6{\cdot}437(1)$, $b = 11{\cdot}298(1)$, $c = 16{\cdot}754(1)$ Å with $Z = 4$. The structure was refined by least squares to R 0·071 for 991 independent reflections. The dehydrated sucrose compound has three extra rings, two on the furanose moiety causing strain about atoms C(3′) and C(4′). The additional ring in the pyranose group causes a change in conformation from the sucrose structure to one with axial hydroxy-groups, and equatorial hydrogen atoms.

ALKALINE degradation of sucrose in sugar milling gives lactic acid as the final product. Richards and O'Donnell[1] have suggested that the mechanism of degradation may involve sucrose anhydrides as intermediates. So far, two trianhydrides have been prepared[2,3] from sucrose; (I) 1′,2: 3,6: 3′,6′-trianhydrosucrose (m.p. 163—164·5 °C, [α] +117° in water), and (II) 3,6-anhydro-α-D-galactosyl-1,4:3,6-dianhydro-β-D-fructoside (m.p. 191—192·5 °C, [α] +137·5° in water).

In attempting to repeat the synthesis of (I), Richards and O'Donnell[1] first isolated the 2,3,4,3′,4′-penta-*O*-acetate of 6,1′,6′-tri-*O*-toluene-*p*-sulphonylsucrose in the pure state. The trianhydride (III), which was obtained in a good yield from purified acetate (m.p. 196—197 °C, $[\alpha]^{32}$ +94°), was different from (I) and (II). Consequently, the structure determination of (III) was undertaken to determine unambiguously the chemical nature of the trianhydride. A brief report has already been published.[4]

DISCUSSION

A stereographic view of (III), which was found to be 3,6-anhydro-α-D-glucosyl-1,4:3,6-dianhydro-β-D-fructoside, is illustrated in Figure 1. The labelling of the atoms is the same as that used by Brown and Levy[5] in their description of sucrose.

The most interesting feature of the molecule is the tricyclic furanose moiety. A comparison with the furanose ring in the neutron-diffraction study of sucrose[4] shows that the strain involved in the formation of this tricyclic structure results in a ' tightening ' of the angles about C(3′) and C(4′), lengthening of the C–O bond distances, and increased puckering of the ring.

All the valence angles in the C(2′), C(3′), C(4′), C(5′), O(2′) ring are smaller than those in sucrose, with the largest differences occurring with the C(3′) and C(4′) valence angles by 12 and 10° respectively. The most distorted angles are C(2′)–C(3′)–C(4′), 90·5(5)°, and C(3′)–C(4′)–C(5′), 92·6(6)°.

The bond distance, C(2′)–O(2′) (1·49 Å) is significantly longer than the corresponding distance (1·41 Å) found in sucrose.

The closure of two additional rings on the furanose part causes the sign of the torsion angle for each of the bonds in the ' primary ' ring [C(2′), C(3′), C(4′), C(5′),

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[1] G. N. Richards and G. W. O'Donnell, 1969, personal communication.

[2] R. U. Lemieux and J. P. Barrette, *J. Amer. Chem. Soc.*, 1958, **80**, 2243.

[3] R. U. Lemieux and J. P. Barrette, *Canad. J. Chem.*, 1959, **37**, 1964.

[4] N. W. Isaccs, C. H. L. Kennard, G. W. O'Donnell, and G. N. Richards, *Chem. Comm.*, 1970, 360.

[5] G. M. Brown and H. A. Levy, *Science*, 1963, **141**, 921, and personal communication.

O(2′)] to be opposite to that in the sucrose molecule[5] and forces the ring into the ‘ half-chair ’ conformation.

The pyranose ring is in the chair form, with the hydroxy-groups axial, and the hydrogen atoms equatorial. This conformation is opposite to that observed in sucrose. As in sucrose, the sign of the torsion angle (Table 1) alternates round the ring, but the magnitudes of the angles are much greater (49—70°) than in sucrose (54·8—56·0°).

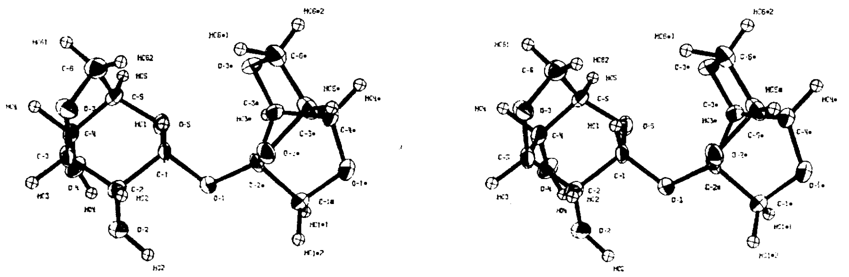
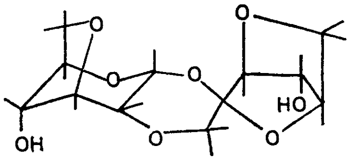
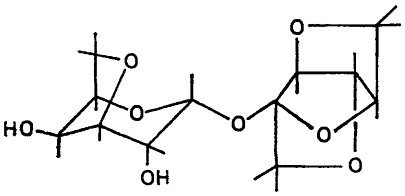


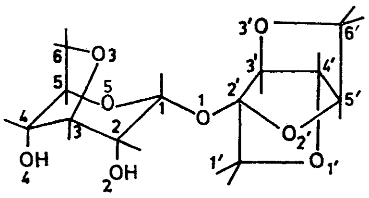
FIGURE 1 Stereographic view of the molecule



(I)



(II)



(III)

TABLE 1

Torsion angles (deg.) *

Pyranose ring		Furanose ring	
C(2)–C(1)	−49·1	C(3′)–C(2′)	55·3
C(3)–C(2)	58·5	C(4′)–C(3′)	−65·4
C(4)–C(3)	−67·3	C(5′)–C(4′)	55·6
C(5)–C(4)	70·2	O(2′)–C(5′)	−21·0
O(5)–C(5)	−68·8	C(2′)–O(2′)	−21·7
C(1)–O(5)	55·0		

* Defined for bond C(3′)–C(2′) as the angle measured counter clock-wise made by the projection of the bond C(3′)–C(4′) relative to the projection of C(2′) and O(2′) when viewed in the direction of C(3′)–C(2′).

The glycosidic link shows some differences from sucrose. While the C(1)–O(1) distances are similar for this compound and sucrose, the O(1)–C(2′) distance (1·372 Å) is significantly shorter (1·43 Å).

The packing of the molecules in the crystal lattice is governed by the hydrogen bonding scheme in which both hydroxy-groups take part. O(2) is hydrogen bonded to O(3′) in the molecule at $x - 1, y, z$, and O(4) is hydrogen bonded to O(1′) in the molecule at $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$, producing a helical-type stacking of molecules along the *a* axis direction. Figure 2 shows this arrangement projected on the *bc* plane.

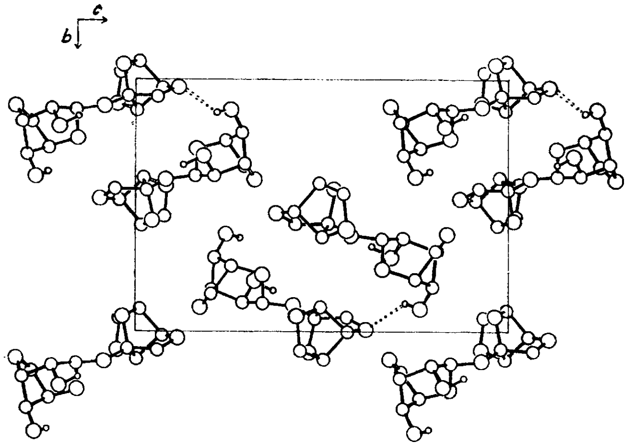


FIGURE 2 Packing of the molecule projected on the *bc* plane

EXPERIMENTAL

Crystal Data.—$C_{12}H_{16}O_8$, $M = 288·2$, Orthorhombic, $a = 6·437(1)$, $b = 11·298(1)$, $c = 16·754(1)$, $U = 1218$ Å^3. $D_m = 1·57$ (by flotation), $Z = 4$, $D_c = 1·57$, $F(000) = 608$, Cu-K_α radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) $= 11·68$ cm^{-1}. Space group, $P2_12_12_1$ (D_2^4, No. 19).

The crystal used (0·4 × 0·25 × 0·2 mm) was mounted with the (100) face perpendicular to the ϕ axis of a Picker four-circle automatic diffractometer. The cell dimensions were obtained by measuring nine axial reflections (200, 400, 600, 020, 040, 060, 002, 004, 008) and refining the three parameters by least squares.

Intensity data up to sin θ 0·90 were collected with nickel-filtered Cu-K_α radiation, using ω—2θ scanning mode. The reflections were scanned at a rate of 1° min^{-1}, and the background scattering was measured with a stationary counter for a period of 20 s on either side of the peak.

TABLE 2

(*a*) Fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	4007(11)	8779(6)	3469(6)
C(2)	2122(11)	8786(6)	2911(5)
C(3)	2839(13)	8293(7)	2096(4)
C(4)	3741(13)	7015(7)	2183(4)
C(5)	5675(12)	7315(7)	2662(4)
C(6)	6499(14)	8367(7)	2165(5)
C(1′)	3533(12)	9318(8)	5652(4)
C(2′)	4532(11)	9350(6)	4823(4)
C(3′)	6735(11)	8845(7)	4993(4)
C(4′)	7067(12)	9775(7)	5660(6)
C(5′)	7020(12)	1·0829(7)	5055(5)
C(6′)	8629(13)	1·0443(8)	4464(5)
O(1)	3202(8)	8903(5)	4260(3)
O(2)	0506(8)	8028(5)	3194(3)
O(3)	4644(8)	8943(5)	1840(3)
O(4)	2409(9)	6122(5)	2475(3)
O(5)	5068(9)	7670(4)	3466(3)
O(1′)	5237(9)	9729(5)	6149(3)
O(2′)	4984(8)	1·0619(4)	4667(3)
O(3′)	8218(8)	9155(5)	4385(3)
H(C1) *	504	953	323
H(C2)	200	980	287
H(C3)	150	843	167
H(C4)	442	690	152
H(C5)	667	656	280
H(1C6)	723	803	165
H(2C6)	696	896	244
H(O2)	−017	840	370
H(O4)	150	629	284
H(1Cl′)	315	849	597
H(2Cl′)	208	993	565
H(C3′)	663	784	508
H(C4′)	858	988	596
H(C5′)	717	1·178	518
H(1C6′)	846	1·078	386
H(2C6′)	1·000	1·055	464

* Hydrogen co-ordinates $\times 10^3$.

(*b*) Thermal parameters † ($\times 10^4$) with estimated standard deviations in parentheses

(i) Anisotropic (β_{ij}/Å^2)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	119(19)	41(6)	9(2)	6(10)	−8(6)	−5(4)
C(2)	111(18)	38(6)	15(3)	9(10)	8(6)	1(4)
C(3)	141(21)	47(7)	11(3)	−13(10)	−10(7)	1(4)
C(4)	145(22)	55(7)	13(3)	−13(11)	−1(6)	−5(4)
C(5)	123(19)	50(6)	12(3)	−6(10)	12(6)	−0(4)
C(6)	145(22)	53(8)	24(4)	−4(12)	4(8)	7(4)
C(1′)	111(20)	74(8)	14(3)	10(12)	5(7)	−6(4)
C(2′)	90(18)	35(6)	14(2)	11(10)	−19(6)	−4(3)
C(3′)	87(19)	50(6)	16(3)	17(10)	3(6)	−4(4)
C(4′)	126(20)	63(8)	12(3)	10(11)	1(7)	−2(4)
C(5′)	118(21)	58(7)	21(3)	−1(11)	−22(7)	3(4)
C(6′)	121(22)	76(9)	20(3)	−3(12)	−12(7)	3(4)
O(1)	94(13)	60(5)	15(2)	−5(8)	−3(5)	−7(3)
O(2)	94(14)	63(5)	21(2)	−7(8)	2(5)	−5(3)
O(3)	112(14)	54(5)	22(2)	−13(8)	−7(5)	15(3)
O(4)	193(17)	44(5)	20(2)	−21(8)	18(5)	−1(3)
O(5)	140(14)	49(4)	12(2)	25(8)	−6(5)	−2(2)
O(1′)	154(16)	69(5)	12(2)	6(9)	−1(5)	−4(3)
O(2′)	125(14)	44(5)	17(2)	16(8)	−16(5)	1(2)
O(3′)	102(14)	67(5)	19(2)	3(8)	13(5)	−8(3)

(ii) Isotropic (B/Å^2)

H(Cl)	1·86	H(O4)	2·70
H(C2)	2·16	H(1Cl′)	2·29
H(C3)	2·23	H(2Cl′)	2·29
H(C4)	2·17	H(C3′)	1·98
H(C5)	2·14	H(C4′)	2·27
H(1C6)	2·67	H(C5′)	2·51
H(2C6)	2·67	H(1C6′)	2·81
H(O2)	2·50	H(2C6′)	2·81

† Defined as $T = \exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

TABLE 3

(*a*) Interatomic distances (Å), with estimated standard deviations in parentheses

C(1)–C(2)	1·53(1)	C(1′)–C(2′)	1·53(1)
C(2)–C(3)	1·54(1)	C(2′)–C(3′)	1·55(1)
C(3)–C(4)	1·56(1)	C(3′)–C(4′)	1·55(1)
C(4)–C(5)	1·52(1)	C(4′)–C(5′)	1·56(1)
C(5)–C(6)	1·55(1)	C(5′)–C(6′)	1·50(1)
O(1)–C(1)	1·429(8)	O(1)–C(2′)	1·372(9)
O(2)–C(2)	1·429(9)	O(1′)–C(1′)	1·453(10)
O(3)–C(3)	1·439(9)	O(1′)–C(4′)	1·436(10)
O(3)–C(6)	1·465(10)	O(2′)–C(2′)	1·486(10)
O(4)–C(4)	1·412(10)	O(2′)–C(5′)	1·483(9)
O(5)–C(1)	1·426(9)	O(3′)–C(3′)	1·440(9)
O(5)–C(5)	1·458(9)	O(3′)–C(6′)	1·481(11)
H(C1)–C(1)	1·15	H(1C1′)–C(1′)	1·10
H(C2) C(2)	1·15	H(2C1′)–C(1′)	1·16
H(C3)–C(3)	1·13	H(C3′)–C(3′)	1·15
H(C4)–C(4)	1·20	H(C4′)–C(4′)	1·10
H(C5)–C(5)	1·09	H(C5′)–C(5′)	1·10
H(1C6)–C(6)	1·05	H(1C6′)–C(6′)	1·09
H(2C6)–C(6)	0·87	H(2C6′)–C(6′)	0·94
H(O2)–O(2)	1·04		
H(O4)–O(4)	0·87		

(*b*) Interatomic angles (deg.)

C(2)–C(1)–O(1)	106·2(5)	C(2′)–C(1′)–O(1′)	101·2(6)
C(2)–C(1)–O(5)	112·4(6)	C(2′)–C(1′)–H(1C1′)	123
O(1)–C(1)–O(5)	105·3(5)	C(2′)–C(1′)–H(2C1′)	109
C(2)–C(1)–H(C1)	104	O(1′)–C(1′)–H(1C1′)	99
O(1)–C(1)–H(C1)	117	O(1′)–C(1′)–H(2C1′)	115
O(5)–C(1)–H(C1)	112	H(1C1′)–C(1′)–H(2C1′)	109
C(1)–C(2)–C(3)	107·5(6)	C(1′)–C(2′)–C(3′)	102·1(6)
C(1)–C(2)–O(2)	111·7(6)	C(1′)–C(2′)–O(1)	110·7(6)
C(3)–C(2)–O(2)	107·2(6)	C(1′)–C(2′)–O(2′)	105·4(6)
C(1)–C(2)–H(C2)	95	C(3′)–C(2′)–O(1)	124·1(6)
C(3)–C(2)–H(C2)	109	C(3′)–C(2′)–O(2′)	102·0(5)
O(2)–C(2)–H(C2)	125	O(1)–C(2′)–O(2′)	110·8(5)
C(2)–C(3)–C(4)	111·2(6)	C(2′)–C(3′)–C(4′)	99·5(5)
C(2)–C(3)–O(3)	108·7(6)	C(2′)–C(3′)–O(3′)	112·7(6)
C(4)–C(3)–O(3)	101·5(6)	C(4′)–C(3′)–O(3′)	104·7(6)
C(2)–C(3)–H(C3)	106	C(2′)–C(3′)–H(C3′)	109
C(4)–C(3)–H(C3)	118	C(4′)–C(3′)–H(C3′)	126
O(3)–C(3)–H(C3)	111	O(3′)–C(3′)–H(C3′)	112
C(3)–C(4)–C(5)	98·5(6)	C(3′)–C(4′)–C(5′)	92·6(6)
C(3)–C(4)–O(4)	117·8(6)	C(3′)–C(4′)–O(1′)	105·9(6)
C(5)–C(4)–O(4)	118·3(6)	C(5′)–C(4′)–O(1′)	112·4(7)
C(3)–C(4)–H(C4)	99	C(3′)–C(4′)–H(C41)	122
C(5)–C(4)–H(C4)	102	C(5′)–C(4′)–H(C4′)	103
O(4)–C(4)–H(C4)	118	O(1′)–C(4′)–H(C41)	118
C(4)–C(5)–C(6)	99·7(6)	C(4′)–C(5′)–C(6′)	101·2(7)
C(4)–C(5)–O(5)	109·3(6)	C(4′)–C(5′)–O(2′)	100·3(6)
C(6)–C(5)–O(5)	112·2(6)	C(6′)–C(5′)–O(2′)	106·0(6)
C(4)–C(5)–H(C5)	115	C(4′)–C(5′)–H(C5′)	128
C(6)–C(5)–H(C5)	121	C(6′)–C(5′)–H(C5′)	111
O(5)–C(5)–H(C5)	100	O(2′)–C(5′)–H(C5′)	109
C(5)–C(6)–O(3)	105·1(6)	C(5′)–C(6′)–O(3′)	102·8(6)
C(5)–C(6)–H(1C6)	109	C(5′)–C(6′)–H(1C6′)	116
C(5)–C(6)–H(2C6)	115	C(5′)–C(6′)–H(2C6′)	114
O(3)–C(6)–H(1C6)	103	O(3′)–C(6′)–H(1C6′)	104
O(3)–C(6)–H(2C6)	98	O(3′)–C(6′)–H(2C6′)	109
H(1C6)–C(6)–H(2C6)	124	H(1C6′)–C(6′)–H(2C6)	110
C(1)–O(1)–C(2′)	116·6(5)	C(1′)–O(1′)–C(4′)	107·7(5)
C(3)–O(3)–C(6)	108·7(5)	C(2′)–O(2′)–C(5′)	104·5(5)
C(5)–O(5)–C(1)	111·9(5)	C(3′)–O(3′)–C(6′)	107·1(6)
C(2)–O(2)–H(O2)	109		
C(4)–O(4)–H(O4)	120		

(*c*) Hydrogen bond distances (Å) and angles (deg.)

O(2) ··· O(3′$^{\mathrm{I}}$)	2·788(1)	C(2)–O(2) ··· O(3′$^{\mathrm{I}}$)	110·6(5)
H(O2) ··· O(3′$^{\mathrm{I}}$)	1·77	O(2)–H(O2) ··· O(3′$^{\mathrm{I}}$)	166
		H(O2)–O(2) ··· O(3′$^{\mathrm{I}}$)	9
O(4) ··· O(1′$^{\mathrm{II}}$)	2·864(7)	C(4)–O(4) ··· O(1′$^{\mathrm{II}}$)	142·7(5)
H(O4) ··· O(1′$^{\mathrm{II}}$)	2·20	O(4)–H(O4) ··· O(1′$^{\mathrm{II}}$)	132
		H(O4)–O(4) ··· O(1′$^{\mathrm{II}}$)	34

Superscripts refer to the equivalent positions:

I $x - 1, y, z$ II $\frac{1}{2} + x, \frac{1}{2} - y, -z$

Of the 1161 reflections scanned 170 were considered to be unobserved. The usual corrections for Lorentz and polarisation factors were made but none for absorption or extinction.

Structure Determination and Refinement.—The structure was solved by direct methods [6] using programs designed by Hall.[7]

Phases were assigned to three linearly independent reflections (2 0 9,$-\pi/2$), (0 5 4,$\pi/2$), and (3 0 7,$-\pi/2$) to define the origin and to a fourth reflection (0 3 15,$\pi/2$) to define the enantiomorph.

The Σ_1 relationship [8] was used to determine the phases of ten zero-layer reflections. With these, the remaining phases of the 271 reflections with $|E| > 1{\cdot}2$ were estimated, and refined using the tangent formula following the procedure of Oh and Maslen.[9]

In an E-map, computed with the 271 phased E values as Fourier coefficients, the complete molecule was revealed. A structure-factor calculation, based on the revealed molecule, gave R 0·21.

Three cycles of full-matrix least-squares refinement, with individual isotropic temperature factors, and unit weights, reduced R to 0·093, and R' $\{=[\Sigma w|F_o - F_c|^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ to 0·107. Three further cycles of refinement with anisotropic temperature factors reduced R to 0·074 and R' to 0·092. When hydrogen atoms located from a difference Fourier map were included, R was reduced to 0·071 and R' to 0·083 after a further four cycles.

In the final refinement, individual reflections were given weights based on their counting statistics, *i.e.* $\sigma^2 = (I_0 - I_B)^{\frac{1}{2}}KF/2(I_0 - I_B)$ where KF = scaled F. The final value for the standard deviation of an observation of unit weight was 4·5. This indicates that the errors were slightly underestimated. Because $w|F_o - F_c|^2$ showed no variation over the full range of F_o and $\sin\theta/y$, there were no gross systematic errors in the data. Similarly a plot of I_0/I_c against I_0 gave no indication of serious extinction effects. The final shift to error ratios were $<0{\cdot}11$ for co-ordinates, and $<0{\cdot}24$ for temperature factors. A difference Fourier map, computed using the final parameters excluding those of H(O4), showed no density $>0{\cdot}4$ eÅ^{-3}. Unfortunately the position of the hydrogen on O(4) was blurred, so that the co-ordinates of this atom H(O4) could only be defined approximately.

The fractional co-ordinates and thermal parameters are shown in Table 2. Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20288 (5 pp., 1 microfiche).* Interatomic distances and angles are tabulated in Table 3.

Calculations.—All calculations [10] were made on a CDC 3600 computer operated by the Computing Research Section of the C.S.I.R.O., Canberra, A.C.T. The scattering factors for carbon and oxygen were taken from ref. 11 and for hydrogen from ref. 12.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

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