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Structure of the Tri-*O*-isopropylidene Derivative of D-Glucosone Hydrate

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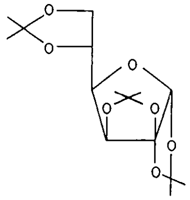
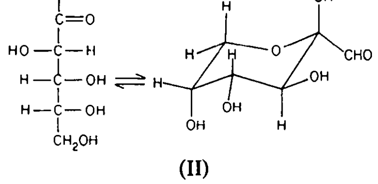
Abstract. 1,2;2,3;5,6-Tri-*O*-isopropylidene-D-*arabino*-hexos-2-ulose hydrate (1,2;2,3;5,6-tri-*O*-isopropylidene-D-glucosone hydrate) (I), $C_{15}H_{24}O_7$, $M_r = 316.35$, m.p. 398 K, $[\alpha]_D^{15°C} = -7°$ (c, 2 g dm^{-3} in methanol), monoclinic, $P2_1$, $a = 8.743$ (1), $b = 10.358$ (2), $c = 9.526$ (1) Å, $\beta = 107.05$ (1)°, $V = 824.7$ Å^3, $Z = 2$, $D_x = 1.274$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ(Mo $K\alpha$) = 0.63 mm^{-1}, $F(000) = 340$, $T = 298$ K, final $R = 0.055$, $wR = 0.056$ for 1495 unique observed ($I > 0$) reflections. The structure determination was undertaken to confirm the structure and stereochemistry of the title compound. The furanoid ring and the 2,3-*O*- and 5,6-*O*-isopropylidene rings have conformations closest to envelopes with C(4), C(10) and C(13), respectively, out of the planes formed by the rest of the rings. The 1,2-*O*-isopropylidene ring has a twist conformation with C(7) and O(2) out of plane.

Experimental. The material (I) was synthesized from D-glucose *via* D-glucosone (II) with retention of chirality following the method of Bayne, Collie & Fewster (1952) and crystallized (colourless prisms) from ether–hexane. Crystal dimensions approximately 0.5 × 0.3 × 0.1 mm. Lattice parameters refined using 25 reflections in the range $10 < \theta < 15°$. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Intensity data collected with $\omega/2\theta$ scan technique ($2 < \theta < 25°$) on 1637 reflections [1495 unique reflections ($I > 0$), $-10 \le h \le 10$, $k \le 12$, $l \le 11$]. Two standard reflections (324 and $\bar{2}16$) showed no decay. The data were corrected for Lorentz and polarization effects; no corrections for absorption or extinction. The structure was solved by direct methods using *SHELXS*84 (Sheldrick, 1983) (default setting). Scattering factors from *International Tables for X-ray Crystallography* (1974). The structure was refined by full-matrix least-squares procedure minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma(F)]^{-2}$. The full-matrix least-squares program *SHELX*76 (Sheldrick, 1976) was used. Since a difference Fourier synthesis did not reveal the positions of all the hydrogen atoms, all H atoms were included in ideal calculated positions in a riding model (all C—H = 1.08 Å). A common isotropic temperature factor refined to 0.070 (5) Å^2. The methyl groups in the isopropylidene rings were refined as rigid groups free to rotate. Refinement with non-hydrogen atoms treated anisotropically converged at $R = 0.055$ and $wR = 0.056$. When the refinement was terminated all shift/e.s.d. ratios were less than 0.02, except those of the rotation parameters of the methyl groups, of which the highest was 0.08. A final difference Fourier synthesis showed $\Delta\rho = \pm 0.3$ e Å^{-3}.



(I)



(II)

Table 1. *Atomic fractional coordinates* ($\times 10^4$) *and* U_{eq} ($\text{Å}^2 \times 10^3$) *for the non-*H *atoms*

U_{eq} is defined as the geometric mean of the diagonal elements of the diagonalized matrix of U_{ij}.

	x	y	z	U_{eq}
O(1)	9236 (5)	9738	10764 (5)	34 (3)
O(2)	6738 (5)	8779 (7)	10222 (5)	36 (3)
O(3)	7268 (5)	7384 (5)	8581 (5)	32 (3)
O(4)	8233 (5)	8942 (7)	7265 (5)	37 (3)
O(5)	10864 (5)	8874 (7)	8588 (4)	34 (3)
O(6)	13037 (5)	8047 (7)	11962 (5)	39 (3)
O(7)	13111 (5)	8709 (8)	14237 (5)	48 (3)
C(1)	7829 (7)	9442 (9)	9654 (7)	32 (4)
C(2)	8276 (7)	8432 (8)	8638 (8)	31 (4)
C(3)	10045 (7)	8113 (9)	9400 (7)	29 (4)
C(4)	10296 (7)	8635 (8)	10944 (7)	30 (4)
C(5)	11962 (8)	9135 (9)	11747 (7)	34 (4)
C(6)	12088 (8)	9627 (9)	13296 (7)	43 (4)
C(7)	6027 (7)	7763 (9)	9212 (8)	36 (4)
C(8)	5668 (9)	6644 (10)	10075 (9)	51 (5)
C(9)	4593 (8)	8269 (10)	8043 (9)	55 (5)
C(10)	9834 (7)	8938 (10)	7120 (7)	38 (4)
C(11)	10051 (9)	7780 (9)	6220 (9)	47 (5)
C(12)	10111 (11)	10237 (9)	6471 (10)	52 (5)
C(13)	14087 (8)	8159 (9)	13433 (8)	40 (4)
C(14)	15498 (8)	9041 (10)	13465 (8)	53 (5)
C(15)	14588 (10)	6812 (10)	14009 (10)	62 (6)

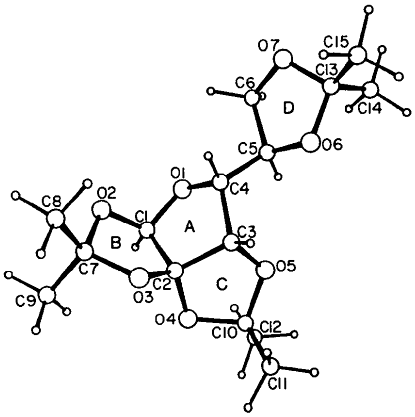


Fig. 1. Perspective view of one molecule of the title compound (I) showing the atom labelling and conformation of the rings. The puckering parameters (Cremer & Pople, 1975) for the four five-membered rings are: *A* ring: $q_2 = 0{\cdot}33$ (1) Å, $\varphi_2 = 209$ (1)°; *B* ring: $q_2 = 0{\cdot}28$ (1) Å, $\varphi_2 = 194$ (1)°; *C* ring: $q_2 = 0{\cdot}31$ (1) Å, $\varphi_2 = 324$ (1)°; *D* ring: $q_2 = 0{\cdot}33$ (1) Å, $\varphi_2 = 172$ (1)°.

Table 1 gives atom parameters and Table 2 bond lengths, angles and endocyclic torsion angles for the non-H atoms.*

Table 2. *Bond distances* (Å), *valency angles* (°) *and endocyclic torsion angles* (°) *for the non-*H *atoms*

O(1)–C(1)	1·400 (7)	O(1)–C(4)	1·449 (7)
O(2)–C(1)	1·406 (7)	O(2)–C(7)	1·439 (7)
O(3)–C(2)	1·389 (7)	O(3)–C(7)	1·441 (7)
O(4)–C(2)	1·401 (8)	O(4)–C(10)	1·446 (7)
O(5)–C(3)	1·434 (7)	O(5)–C(10)	1·426 (7)
O(6)–C(5)	1·443 (8)	O(6)–C(13)	1·437 (8)
O(7)–C(6)	1·429 (8)	O(7)–C(13)	1·421 (8)
C(1)–C(2)	1·552 (9)	C(2)–C(3)	1·540 (8)
C(3)–C(4)	1·522 (8)	C(4)–C(5)	1·524 (8)
C(5)–C(6)	1·534 (9)	C(7)–C(8)	1·507 (10)
C(7)–C(9)	1·506 (8)	C(10)–C(11)	1·518 (10)
C(10)–C(12)	1·529 (10)	C(13)–C(14)	1·529 (9)
C(13)–C(15)	1·516 (11)		

C(1)–O(1)–C(4)	107·8 (5)	C(1)–O(2)–C(7)	108·0 (5)
C(2)–O(3)–C(7)	108·5 (5)	C(2)–O(4)–C(10)	109·1 (5)
C(3)–O(5)–C(10)	106·5 (5)	C(5)–O(6)–C(13)	106·1 (5)
C(6)–O(7)–C(13)	107·1 (5)	O(1)–C(1)–O(2)	111·2 (5)
O(1)–C(1)–C(2)	107·0 (5)	O(2)–C(1)–C(2)	103·6 (5)
O(3)–C(2)–O(4)	114·5 (5)	O(3)–C(2)–C(1)	106·2 (5)
O(4)–C(2)–C(1)	112·7 (6)	O(3)–C(2)–C(3)	112·9 (6)
O(4)–C(2)–C(3)	105·6 (5)	C(1)–C(2)–C(3)	104·6 (5)
O(5)–C(3)–C(2)	102·6 (5)	O(5)–C(3)–C(4)	111·9 (6)
C(2)–C(3)–C(4)	102·7 (5)	O(1)–C(4)–C(3)	105·1 (5)
O(1)–C(4)–C(5)	106·0 (5)	C(3)–C(4)–C(5)	116·9 (5)
O(6)–C(5)–C(4)	107·0 (6)	O(6)–C(5)–C(6)	105·3 (5)
C(4)–C(5)–C(6)	112·6 (6)	O(7)–C(6)–C(5)	103·7 (6)
O(2)–C(7)–O(3)	104·3 (5)	O(2)–C(7)–C(8)	108·4 (6)
O(3)–C(7)–C(8)	108·7 (6)	O(2)–C(7)–C(9)	110·1 (6)
O(3)–C(7)–C(9)	110·6 (6)	C(8)–C(7)–C(9)	114·2 (6)
O(4)–C(10)–O(5)	104·9 (5)	O(4)–C(10)–C(11)	109·9 (6)
O(5)–C(10)–C(11)	111·7 (6)	O(4)–C(10)–C(12)	108·0 (7)
O(5)–C(10)–C(12)	108·0 (6)	C(11)–C(10)–C(12)	114·0 (6)
O(6)–C(13)–O(7)	104·2 (5)	O(6)–C(13)–C(14)	110·4 (6)
O(7)–C(13)–C(14)	111·0 (7)	O(6)–C(13)–C(15)	108·2 (7)
O(7)–C(13)–C(15)	109·2 (7)	C(14)–C(13)–C(15)	113·4 (7)

C(1)–O(1)–C(4)–C(3)	37·1 (7)	O(5)–C(10)–O(4)–C(2)	−20·8 (8)
O(1)–C(4)–C(3)–C(2)	−31·7 (7)	C(10)–O(4)–C(2)–C(3)	1·0 (8)
C(4)–C(3)–C(2)–C(1)	16·0 (7)	O(4)–C(2)–C(3)–O(5)	18·9 (7)
C(3)–C(2)–C(1)–O(1)	5·3 (8)	C(2)–C(3)–O(5)–C(10)	−32·1 (7)
C(2)–C(1)–O(1)–C(4)	−26·2 (7)	C(3)–O(5)–C(10)–O(4)	33·5 (7)
O(3)–C(7)–O(2)–C(1)	31·8 (7)	O(7)–C(13)–O(6)–C(5)	33·8 (8)
C(7)–O(2)–C(1)–C(2)	−24·0 (7)	C(13)–O(6)–C(5)–C(6)	−17·6 (8)
O(2)–C(1)–C(2)–O(3)	7·4 (8)	O(6)–C(5)–C(6)–O(7)	−4·7 (8)
C(1)–C(2)–O(3)–C(7)	12·0 (8)	C(5)–C(6)–O(7)–C(13)	25·9 (8)
C(2)–O(3)–C(7)–O(2)	−26·6 (7)	C(6)–O(7)–C(13)–O(6)	−37·7 (8)

Related literature. Mutagenicity studies of D-glucosone (II) (Niemand, den Drijver, Pretorius, Holzapfel & van der Linde, 1983) required a convenient source of the pure compound (II). Known syntheses (Haas & Schlimmer, 1972; Liu, Wolf, Geigert, Niedleman, Chin & Shirang, 1983; Walton, 1969) do not yield pure (II) on a large scale. Hydrolysis of the readily available and easily purified (I) furnishes an isomer of (II) with inverted stereochemistry at C(3) (den Drijver, 1985) which raised the question of the correctness of the assigned structure of (I). This recent determination shows that the supposed stereochemistry of (I) is correct.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43403 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
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Diphenyl(2,2-diphenylvinyloxy)acetaldehyde

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Abstract. $C_{28}H_{22}O_2$, $M_r = 390{\cdot}49$, triclinic, $P\bar{1}$, $a = 9{\cdot}604\,(5)$, $b = 10{\cdot}567\,(8)$, $c = 11{\cdot}346\,(9)$ Å, $\alpha = 79{\cdot}89\,(6)$, $\beta = 72{\cdot}79\,(6)$, $\gamma = 78{\cdot}54\,(6)°$, $V = 1070\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}212$ Mg m^{-3}, $F(000) = 412$, $\lambda(\text{Ag}\,K\alpha) = 0{\cdot}5608$ Å, $\mu = 0{\cdot}05$ mm^{-1}, $T = 291\,(1)$ K, final $R = 0{\cdot}038$, for 1865 unique observed X-ray diffractometer data and 272 variables. The compound is the first and unexpected example of a reversible dimerization of diphenylmethyl radicals of the kind $Ph_2C^{\cdot}$—CO—R using their enoxyl form, and yielding a strainless new type of enol ether.

Experimental. The substance (Neumann & Stapel, 1986) was crystallized from a boiling mixture of benzene/petroleum ether (333–363 K) (1:1) by slow cooling to 277 K.

Crystal size 0·22 × 0·42 × 0·42 mm, $\omega/2\theta$ scan, scan speed 2·9–6·7° min^{-1} in θ, Nonius CAD-4 diffractometer, graphite-monochromated Ag $K\alpha$; lattice parameters from least-squares fit with 25 reflections up to $2\theta = 25{\cdot}6°$; five standard reflections recorded every 2·5 h, only random deviations; 8232 reflections measured; $1 \leq \theta \leq 20°$, $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$; after averaging ($R_{\text{int}} = 0{\cdot}023$): 4044 unique reflections, 1865 with $I > 1{\cdot}96\sigma(I)$; Lorentz–polarization correction, no absorption correction; space group $P\bar{1}$; structure solution *via* direct methods, ΔF syntheses and full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C—H 0·95 Å); refinement on F with 1865 reflections and 272 refined parameters; $w = 4F_o^2/[\sigma^2(F_o^2) + 0{\cdot}06F_o^2]^2$; $S = 0{\cdot}95$, $R = 0{\cdot}038$, $wR = 0{\cdot}046$, $(\Delta/\sigma)_{\max} = 0{\cdot}01$; no extinction correction; largest peak in final ΔF map $\pm 0{\cdot}13\,(7)$ e Å^{-3}; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); programs: *Enraf–Nonius Structure Determination Package* (Frenz, 1981), *ORTEP*II (Johnson, 1976), *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *POP*1 (van de Waal, 1976).

Table 1 contains final atom coordinates and equivalent isotropic thermal parameters for non-hydrogen

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^3)

$$U_{\text{eq}} = (1/24\pi^2)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0·7334 (2)	0·1757 (1)	0·3689 (1)	50
O(2)	0·4390 (2)	0·1821 (2)	0·4381 (2)	65
C(1)	0·6686 (2)	0·1454 (2)	0·2804 (2)	44
C(2)	0·7395 (3)	0·0857 (2)	0·4708 (2)	46
C(3)	0·7602 (2)	0·1171 (2)	0·5720 (2)	43
C(4)	0·5020 (3)	0·1567 (2)	0·3357 (2)	51
C(11)	0·6901 (3)	0·2543 (2)	0·1719 (2)	45
C(12)	0·6489 (3)	0·2465 (2)	0·0668 (2)	59
C(13)	0·6620 (3)	0·3462 (3)	−0·0302 (2)	70
C(14)	0·7172 (4)	0·4523 (3)	−0·0253 (3)	83
C(15)	0·7588 (4)	0·4600 (3)	0·0779 (3)	100
C(16)	0·7449 (3)	0·3631 (3)	0·1765 (2)	74
C(21)	0·7376 (2)	0·0122 (2)	0·2393 (2)	41
C(22)	0·6610 (3)	−0·0921 (2)	0·2689 (2)	55
C(23)	0·7309 (3)	−0·2123 (2)	0·2334 (3)	67
C(24)	0·8765 (3)	−0·2299 (3)	0·1696 (2)	66
C(25)	0·9534 (3)	−0·1281 (3)	0·1400 (2)	63
C(26)	0·8848 (3)	−0·0076 (2)	0·1744 (2)	54
C(31)	0·7634 (3)	0·2531 (2)	0·5873 (2)	46
C(32)	0·6498 (3)	0·3510 (3)	0·5708 (3)	79
C(33)	0·6522 (4)	0·4772 (3)	0·5853 (3)	106
C(34)	0·7692 (4)	0·5079 (3)	0·6139 (3)	87
C(35)	0·8804 (3)	0·4123 (3)	0·6324 (2)	68
C(36)	0·8777 (3)	0·2852 (2)	0·6203 (2)	54
C(41)	0·7802 (2)	0·0117 (2)	0·6738 (2)	44
C(42)	0·7131 (3)	0·0298 (2)	0·7975 (2)	55
C(43)	0·7251 (3)	−0·0701 (3)	0·8914 (2)	71
C(44)	0·8035 (3)	−0·1889 (3)	0·8654 (2)	75
C(45)	0·8732 (3)	−0·2087 (3)	0·7439 (3)	69
C(46)	0·8623 (3)	−0·1092 (2)	0·6492 (2)	54

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