1,2-O-Isopropylidene-D-glucofuranose*

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Abstract. $C_9H_{16}O_6$, $M_r = 220.22$, m.p. 433 K, monoclinic $P2_1$, $a = 5.604$ (1), $b = 9.641$ (1), $c = 19.383$ (1) Å, $\beta = 90.70$ (2)°, $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å, $V = 1047.1$ Å³, $D_x = 1.397$ Mg m⁻³, $Z = 4$. The structure was solved by direct methods and refined to $R(F) = 0.026$ for 2344 symmetry-averaged reflections. The two symmetry-independent molecules have very similar molecular dimensions, except for the orientation of the two hydroxyl groups. The acetal moiety C(7)–O(1)–C(1)–O(4)–C(4) has bond lengths (mean) of 1.436, 1.400, 1.421, 1.449 Å, showing variations similar to those observed and predicted theoretically for the methyl pyranosides. The hydrogen bonding involves four unsymmetrical bifurcated interactions.

Introduction. 1,2-O-Isopropylidene-D-glucofuranose (I) was obtained from Aldrich Chemical Co., Inc. and recrystallized from 95% ethanol–water solution at room temperature. A crystal with dimensions 0.20 × 0.22 × 0.34 mm was used to collect 5451 intensities of the type hkl, $\bar{h}kl$, $\bar{h}k\bar{l}$ and $hk\bar{l}$ by θ–2θ scans to $\theta = 78°$ on a CAD-4 X-ray diffractometer using a scan width of $3.06° + 0.42° \tan \theta$. Absorption corrections [$\mu(\text{Cu } K\alpha) = 0.965$ mm⁻¹] were applied with *ABSOR* (Templeton & Templeton, 1973). The maximum and minimum absorption corrections to F_o^2 were 1.284 and

1.185 respectively. The R factor between symmetry-equivalent reflections was 0.013. The reflections were averaged to 2344 symmetry-independent structure amplitudes.
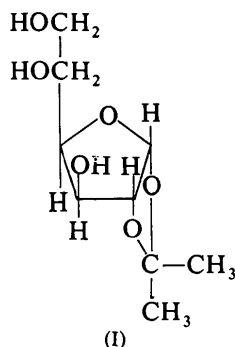
The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) using 200 reflections for phase generation. The first E map revealed 28 of the 30 non-hydrogen atoms. Refinement was by least squares using *FLIN* 80, a local version of *ORFLS* (Busing, Martin & Levy, 1962) to minimize $\sum w|F_o - kF_c|^2$ with

HOCH₂
|
HOCH₂
|

(I)

Table 1. *Atomic coordinates* ($\times 10^4$) *for non-hydrogen atoms in* 1,2-O-isopropylidene-D-glucofuranose

Estimated standard deviations are given in parentheses.

	x	y	z
Molecule (1)			
C(1)	3423 (3)	4231 (2)	5790 (1)
C(2)	5668 (3)	3456 (2)	5568 (1)
C(3)	6542 (3)	2763 (2)	6229 (1)
C(4)	4180 (2)	2455 (2)	6581 (1)
C(5)	4362 (3)	2210 (2)	7355 (1)
C(6)	1951 (3)	1997 (3)	7684 (1)
C(7)	2671 (3)	3023 (2)	4777 (1)
C(8)	3305 (5)	3899 (3)	4159 (1)
C(9)	940 (4)	1880 (3)	4616 (1)
O(1)	1665 (2)	3899 (2)	5299 (1)
O(2)	4768 (2)	2454 (2)	5092 (1)
O(3)	7824 (2)	3739 (2)	6630 (1)
O(4)	2797 (2)	3697†	6448 (1)
O(5)	5878 (2)	1035 (2)	7465 (1)
O(6)	787 (2)	839 (2)	7380 (1)
Molecule (2)			
C(1*)	3248 (3)	4692 (2)	−812 (1)
C(2*)	5541 (3)	5436 (2)	−586 (1)
C(3*)	6352 (3)	6150 (2)	−1244 (1)
C(4*)	3956 (2)	6484 (2)	−1584 (1)
C(5*)	4028 (3)	6796 (2)	−2354 (1)
C(6*)	1563 (3)	6969 (3)	−2672 (1)
C(7*)	2646 (3)	5860 (2)	213 (1)
C(8*)	3329 (5)	4923 (3)	811 (1)
C(9*)	977 (4)	7000 (3)	406 (1)
O(1*)	1538 (2)	5045 (2)	−320 (1)
O(2*)	4721 (2)	6429 (2)	−97 (1)
O(3*)	7566 (2)	5179 (2)	−1657 (1)
O(4*)	2588 (2)	5230 (2)	−1469 (1)
O(5*)	5270 (2)	8077 (2)	−2444 (1)
O(6*)	176 (2)	7995 (2)	−2322 (1)

† Fixed by crystal symmetry.

$w^{-1} = [\sigma_c^2(F_o^2) + (0 \cdot 022F_o^2)^2]/4F_o^2$, where σ_c is from counting statistics. All H atoms were located from difference syntheses and refined isotropically. A Zachariasen isotropic extinction parameter (Coppens & Hamilton, 1970) was included and refined to a value of

Table 2. *Fractional atomic parameters* $(\times 10^3)$ *and bond distances* (Å) *for hydrogen atoms in 1,2-O-isopropylidene-D-glucofuranose*

	x	y	z	C, O–H
Molecule (1)				
H(C1)	356 (3)	527 (2)	584 (1)	1·01 (2)
H(C2)	687 (4)	412 (3)	535 (1)	1·02 (2)
H(C3)	749 (3)	189 (2)	615 (1)	1·01 (2)
H(C4)	336 (3)	168 (2)	636 (1)	0·97 (2)
H(C5)	514 (4)	303 (2)	757 (1)	0·99 (2)
H(C61)	94 (4)	277 (3)	762 (1)	0·94 (2)
H(C62)	223 (5)	179 (3)	821 (1)	1·05 (2)
H(C81)	452 (7)	470 (5)	431 (2)	1·07 (4)
H(C82)	191 (7)	430 (5)	398 (2)	0·94 (4)
H(C83)	411 (5)	326 (3)	384 (1)	0·99 (3)
H(C91)	−54 (5)	222 (4)	449 (1)	0·92 (3)
H(C92)	83 (5)	137 (3)	503 (1)	0·94 (3)
H(C93)	167 (5)	137 (3)	425 (1)	0·96 (3)
H(O3)	931 (5)	366 (3)	651 (1)	0·87 (3)
H(O5)	514 (5)	40 (3)	740 (1)	0·75 (3)
H(O6)	−58 (4)	96 (3)	738 (1)	0·77 (2)
Molecule (2)				
H(C1*)	338 (4)	364 (3)	−84 (1)	1·02 (2)
H(C2*)	677 (4)	487 (2)	−40 (1)	0·95 (2)
H(C3*)	736 (3)	692 (2)	−115 (1)	0·95 (2)
H(C4*)	326 (3)	723 (2)	−136 (1)	0·93 (2)
H(C5*)	483 (3)	603 (2)	−258 (1)	0·97 (2)
H(C61*)	73 (4)	613 (3)	−264 (1)	0·94 (3)
H(C62*)	171 (4)	730 (3)	−317 (1)	1·02 (2)
H(C81*)	199 (6)	453 (4)	101 (2)	0·93 (4)
H(C82*)	400 (6)	547 (4)	117 (2)	0·95 (3)
H(C83*)	436 (7)	415 (4)	59 (2)	1·04 (4)
H(C91*)	72 (5)	760 (4)	−0 (2)	0·99 (3)
H(C92*)	−67 (5)	656 (3)	52 (1)	1·04 (3)
H(C93*)	176 (5)	753 (4)	77 (1)	0·97 (3)
H(O3*)	900 (4)	527 (3)	−157 (1)	0·82 (2)
H(O5*)	672 (4)	789 (3)	−240 (1)	0·84 (2)
H(O6*)	80 (5)	875 (3)	−242 (1)	0·83 (3)

$0 \cdot 26$ (3) $\times$ 10^4. The final values of $R = \sum |F_o - kF_c|/\sum |F_o|$, $R_w = [\sum w|F_o - kF_c|^2/\sum F_o^2]^{1/2}$ were $0 \cdot 026$ and $0 \cdot 034$, respectively, for all 2344 reflections.

The atomic scattering factors for C and O were those of Doyle & Turner (1968) and of Stewart, Davidson & Simpson (1965) for H. The atomic parameters are given in Tables 1 and 2.†

Discussion. The atomic notation and thermal ellipsoids are shown in Fig. 1. The bond lengths, valence angles and principal torsion angles for non-H atoms are given in Fig. 2 for the two symmetry-independent molecules. The calculation of distances and angles with their estimated standard deviations was made using the variance–covariance matrix (Busing, Martin & Levy, 1964). The σ's for the bond lengths were $0 \cdot 002$ Å and for bond angles and torsion angles $0 \cdot 1°$, except for $0 \cdot 003$ Å for C(6)–O(6) and C(6*)–O(6*), and $0 \cdot 2°$ for

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34255 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 2. Molecular dimensions (Å and deg) of 1,2-*O*-isopropylidene-D-glucofuranose. (*a*) Bond lengths and selected torsion angles, molecule (1), (*b*) bond lengths and selected torsion angles, molecule (2), (*c*) valence angles, molecule (1), (*d*) valence angles, molecule (2).
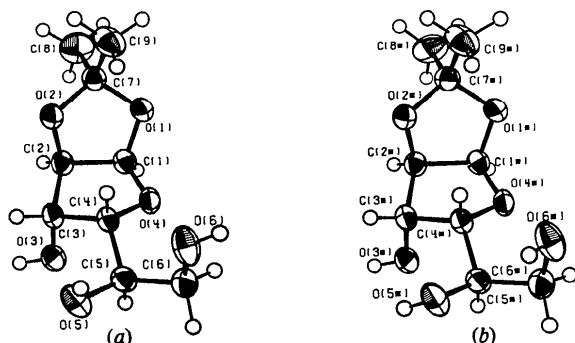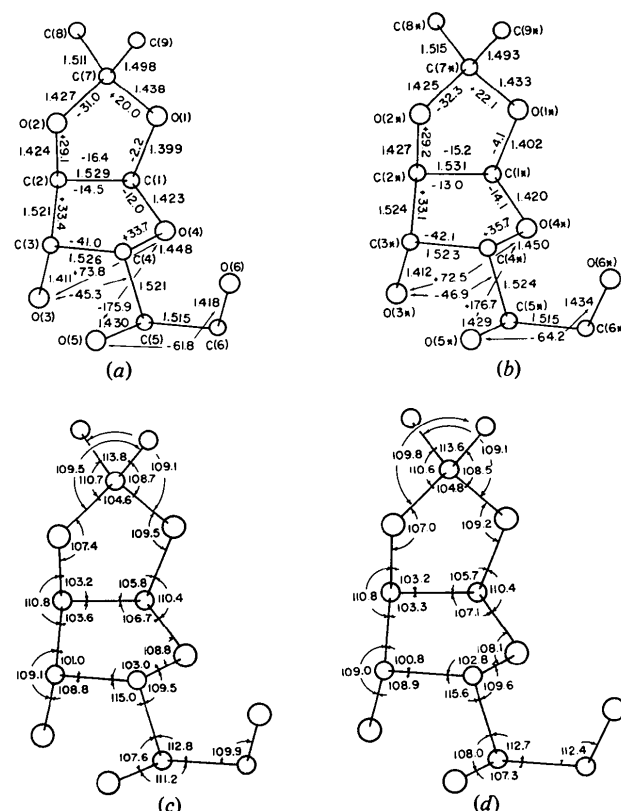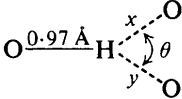

Fig. 1. 1,2-*O*-Isopropylidene-D-glucofuranose. Atomic notation and thermal ellipsoids at 50% probability (Johnson, 1976). (*a*) molecule (1), (*b*) molecule (2).

angles involving C(7) and C(7*). The major differences in the conformations of the two molecules occur only in the orientation of the O(5)—H and O(6)—H bonds. In both molecules, the glucofuranose ring has the $^3T_4$ ($\varphi =$ 306°) conformation with almost identical Cremer & Pople (1975) puckering parameters: $Q =$ 0·398, 0·408 Å, $\varphi =$ 303, 305°. The dioxalane rings are closer to the $^{O(2)}E$ conformation ($\varphi =$ 288°) with puckering parameters of $Q =$ 0·283, 0·291 Å, $\varphi =$ 291, 294°. [The notation is taken clockwise with O(1) as atom 1 in the Cremer—Pople program.] The largest difference in a ring torsional angle between the two molecules is only 2·1°, indicating that the two-fused-ring system is rigid and only slightly affected by the crystal-field forces. The angles between the two five-membered rings, defined by the torsion angle O(2)—C(2)—C(1)—O(4), are +101 and +102° for molecules (1) and (2) respectively.

The C—O bond lengths in the acetal sequence C(4)—O(4)—C(1)—O(1)—C(7) show the characteristic bond-length variations observed in the methyl pyranosides and predicted from theoretical calculations (Jeffrey, Pople, Binkley & Vishveshwara, 1978), although the C(4)—O(4)—C(1)—O(1) and O(4)—C(1)—O(1)—C(7) torsion angles of +102, 100° and −117, −120° are different from the angles close to 60 or 180° observed in the acetal moiety of the pyranosides.

The hydrogen bonding is shown in Fig. 3, and a stereoview showing molecular packing is given in Fig. 4. The hydrogen bonding is unusual since it includes

Table 3. *The geometry of the bifurcated bonds in the crystal structure of* 1,2-O-isopropylidene-D-gluco-furanose *with normalized O—H bond lengths*

	x	y	θ
O(3)H to O(1) and O(4)	1·86 Å	2·65 Å	59°
O(3*)H to O(1*) and O(4*)	1·87	2·71	57
O(5)H to O(5*) and O(6)	2·10	2·40	110
O(6*)H to O(5*) and O(6)	1·93	2·57	109

Some comparable neutron diffraction data on bifurcated bonds

β-D-Fructopyranose	1·965	2·349	92
(Takagi & Jeffrey, 1977)	1·977	2·593	75
β-L-Lyxopyranose	1·957	2·300†	106
(Nordenson, Takagi & Jeffrey, 1978)	2·113	2·634	91
Methyl β-D-ribopyranoside	1·958	2·568	125
(James, Stevens & Moore, 1978)	1·989	2·498	77
	1·947	2·696	111
α-L-Sorbopyranose	1·953	2·582	73
(Nordenson, Takagi & Jeffrey, 1979)	2·151	2·209	81
α-L-Rhamnopyranose	1·949	2·715	120
(Takagi & Jeffrey, 1978)			

† Intramolecular interaction.

one symmetrical and three unsymmetrical interactions, the geometries of which are given in Table 3. When the O—H covalent-bond lengths are normalized to a standard neutron diffraction value of 0·97 Å, the geometries of these unsymmetrical bifurcated inter-actions are in good agreement with those observed in other monosaccharide structures studied by neutron diffraction methods, as shown in Table 3. The energetics of symmetrical and unsymmetrical bifur-cated hydrogen bonds *versus* linear hydrogen bonds have been studied by *ab initio* MO methods by Newton, Jeffrey & Takagi (1979). Their results indicate that such interactions can be energetically favorable and that hydrogen bonding such as observed in this structure may be more common than hitherto realized.
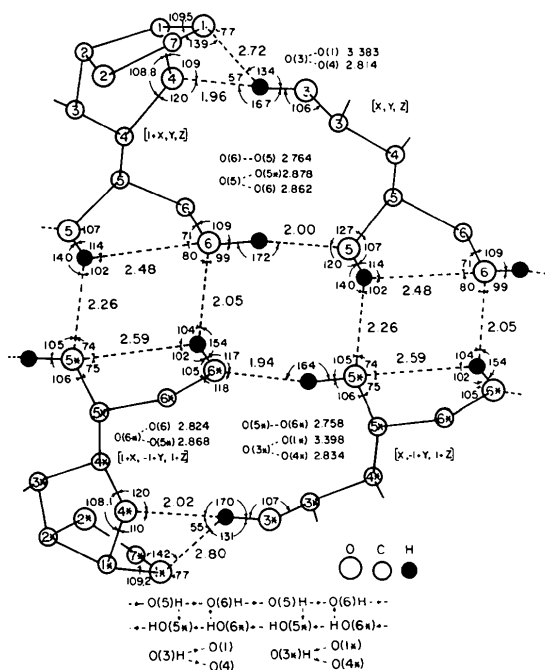

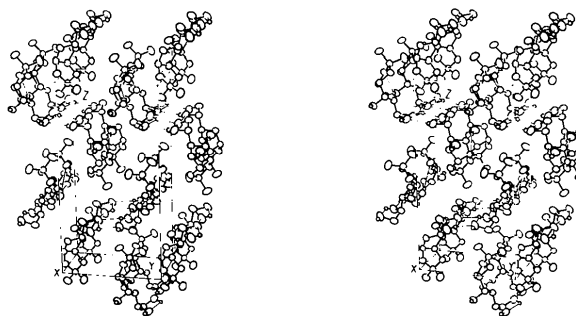Fig. 3. The hydrogen bonding in the crystal structure of 1,2-O-isopropylidene-D-glucofuranose.

Fig. 4. Molecular packing in 1,2-O-isopropylidene-D-glucofuranose. Thermal ellipsoids are at 50% probability (Johnson, 1976).

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O,N-Diacétate de l'Enol de Colchicine

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Abstract. $C_{26}H_{29}NO_8$, monoclinic, $C2/c$, $a = 23\cdot71$ (2), $b = 10\cdot827$ (5), $c = 19\cdot29$ (1) Å, $\beta = 103\cdot0$ (1)°, $Z = 8$, $D_c = 1\cdot41$ Mg m⁻³. The structure was solved by direct methods and refined to an R of $0\cdot045$ for 4440 unique diffraction data. Puckering and junction angles of rings B and C are quite different from those of the natural colchicine.

Introduction. La colchicine (1) est un dérivé extrait de crocus (*Colchicum automnale*) qui présente une grande variété d'activités biologiques. On peut considérer que la plus intéressante est son activité antimitotique par inhibition de la formation de microtubules. Ceci explique aussi son activité anti-inflammatoire (Fitzgerald, 1974).

Plusieurs dérivés ont été synthétisés (Blade-Font, 1977*a,b*) pour essayer d'améliorer les qualités biologiques. Pour établir avec certitude la structure des molécules synthétisées et la géométrie du système heptafulvénique une analyse radiocristallographique de

l'*O,N*-diacétate de l'énol de colchicine (2) s'est avérée nécessaire (Fig. 1).

Les cristaux jaunes sont obtenus par évaporation d'une solution dans l'acétate d'éthyle. Les données ont été collectées avec un cristal (0,2 × 0,2 × 0,1 mm) sur un diffractomètre utilisant la raie $K\bar{\alpha}$ du cuivre ($\lambda = 1,54178$ Å). Sur 4440 réflexions mesurées, 3923 sont considérées comme observées [$I > 2\sigma(I)$].

La structure a été déterminée par méthodes directes à l'aide du programme *SIR* (Giacovazzo, 1977; Busetta, 1978). La carte de densité électronique calculée avec les phases de 318 réflexions ($E > 1,80$) de la meilleure solution a permis de localiser tous les atomes autres que les atomes d'hydrogène. L'affinement par moindres carrés des positions et des facteurs thermiques a utilisé l'approximation des blocs diagonaux. Les atomes d'hydrogène ont été localisés sur des séries de Fourier 'différences'. L'affinement final des positions atomiques, des facteurs thermiques anisotropes pour les atomes C, N, O et isotropes pour les