Acta Cryst. (1980). B36, 2730–2733

Structure and Molecular Conformation of 1-(4-Acetyl-5-methyl-2-furyl)-1,3-dideoxy-3-nitro-β-D-xylopyranose

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(*Received* 9 *April* 1980; *accepted* 27 *June* 1980)

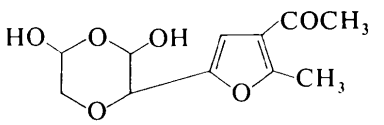
Abstract

The crystal structure of $C_{12}H_{15}NO_7$ has been determined at room temperature. Crystals are tetragonal, space group $P4_32_12$, $Z = 8$, with $a = 12{\cdot}039$ (1), $c = 17{\cdot}979$ (4) A. 1304 observed reflexions contributed to the full-matrix least-squares refinement to give $R = 0{\cdot}075$. The pyranose ring displays a slightly distorted chair with $^4C_1$ conformation and all the substituents (furanose ring, NO_2 and OH groups) are equatorial. The reported configuration can be considered as the absolute configuration from the absence of epimerization at the anomeric atom. The packing of the structure can be described by a three-dimensional hydrogen-bonding scheme.

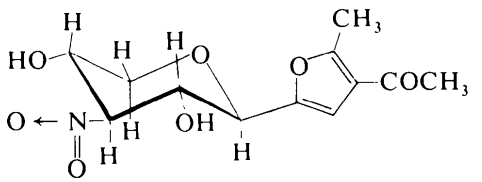
Introduction

C-glycosides is the term used for compounds analogous to glycosides in which the anomeric carbon atom is bonded to a carbon atom of the aglycone group. In these compounds the anomeric carbon is not acetalic and displays different characteristics to that in *O*-glycosides and *N*-glycosides.

By Baer–Fisher reaction of 2-(*R*)-(4-acetyl-5-methyl-2-furyl)-3,5-dihydroxy-1,4-dioxane (I), two isomers with molecular formula $C_{12}H_{15}NO_7$ were isolated. From IR and NMR spectroscopic data the $^4C_1$ conformation for the pyranose ring, and β-D-xylo (II) and α-L-arabino (III) configurations, respectively, were considered as probable structures (Asenjo-Asenjo, 1979). The β-D-xylo isomer was obtained in crystalline form but the α-L-arabino form was non-crystalline.



(I)



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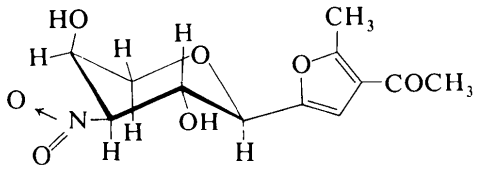

(III)

Because of the existence of four chiral centres in the molecule and in order to elucidate completely the conformational and configurational details, an X-ray study of (II) was suggested by Professor J. López-Aparicio of the Organic Chemistry Department, University of Granada.

Experimental

Colourless prismatic crystals of the title compound suitable for X-ray analysis were kindly supplied by Professor López-Aparicio. Preliminary oscillation and Weissenberg photographs indicated tetragonal symmetry and the observed conditions for reflexions ($00l$, $l = 4n$; $h00$, $h = 2n$) were consistent with the space groups $P4_12_12$ and $P4_32_12$. $P4_32_12$ was chosen. Cell parameters [$a = b = 12{\cdot}039$ (1), $c = 17{\cdot}979$ (4) Å] were obtained by least-squares refinement from 45 reflexions. Other crystal data are: $V = 2605{\cdot}8$ (6) Å^3, $Z = 8$, m.p. = 460 (5) K, $D_m = 1{\cdot}44$ (1), $D_x = 1{\cdot}45$ Mg m^{-3}, $F(000) = 1200$, μ(Cu $K\alpha$) = 0·99 mm^{-1}.

Diffraction data were collected on a Philips automated four-circle diffractometer equipped with a graphite monochromator and operated in the ω–2θ scan mode. The background was measured at either end of the scan and two reflexions were monitored after each 50 measurements during the data collection. Of the 1304 independent reflexions accessible with Cu $K\alpha$ radiation in the range $2 < \theta < 65°$, 1288 had significant intensities [$I > 2\sigma(I)$] and were considered as observed. Data were corrected in the usual way for Lorentz and polarization effects, but not for absorption or extinction.

Structure determination

The structure was solved by multisolution weighted-tangent-formula refinement (*MULTAN*: Main, Les-

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singer, Woolfson, Germain & Declercq, 1977) of 182 reflexions with $|E| > 1.40$ (approximately nine reflexions per non-hydrogen atom in the asymmetric unit). An E map computed with the phase set of the highest combined figure of merit revealed the positions of 17 atoms of the molecule. All the remaining non-hydrogen atoms were located on a Fourier synthesis computed with the phase set of the known atoms.

The structure was refined by full-matrix least-squares methods (*CRYLSQ*: Stewart, Kundell & Baldwin, 1970), minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Refinement of the model with anisotropic thermal parameters resulted in $R = 0.095$. At this stage a difference Fourier synthesis revealed the H atoms with expected geometry. Two additional cycles of full-matrix least-squares refinement in which each H atom was assigned an isotropic thermal parameter (4 Å^2) led to final convergence with $R = 0.075$. All parameter shifts during the final cycle of refinement were less than 0.5σ. The overdetermination ratio n/m, where n is the number of reflexions used in the refinement and m is the number of refined parameters, was 5·7. The final positional parameters are listed in Table 1. Equivalent isotropic temperature factors were calculated by averaging the three diagonal anisotropic thermal parameters.*

Table 1. *Atomic coordinates* ($\times 10^4$ *for non-hydrogen*, $\times 10^3$ *for hydrogen atoms*) *and isotropic temperature factors*

H atoms were assigned a B value of 4 Å^2.

	x	y	z	B (Å^2)
O(1)	6473 (6)	−922 (5)	−4589 (3)	2·7
O(2)	7740 (6)	1792 (5)	−4988 (3)	2·9
O(3)	9436 (6)	−8 (7)	−5938 (4)	4·9
O(4)	8589 (7)	1124 (7)	−6671 (4)	5·2
O(5)	7010 (7)	−1229 (6)	−6592 (3)	3·5
O(6)	7643 (6)	−152 (6)	−3365 (3)	3·5
O(7)	7283 (8)	1306 (7)	−1254 (4)	4·9
N	8606 (7)	461 (7)	−6160 (4)	2·8
C(1)	6616 (8)	245 (7)	−4518 (4)	2·5
C(2)	7658 (8)	619 (7)	−4956 (4)	2·2
C(3)	7519 (8)	230 (8)	−5771 (4)	2·2
C(4)	7268 (9)	−1008 (8)	−5822 (4)	3·1
C(5)	6217 (9)	−1236 (9)	−5343 (4)	3·4
C(6)	6769 (8)	478 (8)	−3700 (4)	2·4
C(7)	7675 (10)	182 (10)	−2638 (5)	3·7
C(8)	6896 (8)	956 (8)	−2520 (5)	2·8
C(9)	6269 (9)	1159 (9)	−3223 (5)	3·8
C(10)	8506 (9)	−435 (11)	−2148 (6)	5·7
C(11)	6713 (11)	1514 (11)	−1789 (6)	5·3
C(12)	5777 (12)	2333 (13)	−1776 (7)	4·3
H(1)	582 (12)	63 (12)	−470 (7)	
H(2)	838 (12)	24 (13)	−469 (7)	
H(3)	681 (12)	61 (13)	−603 (8)	
H(4)	795 (13)	−158 (12)	−562 (7)	
H(51)	598 (12)	−202 (13)	−537 (8)	
H(52)	547 (12)	−79 (12)	−555 (8)	
H(9)	566 (13)	162 (13)	−333 (8)	
H(101)	831 (12)	−128 (13)	−217 (8)	
H(102)	927 (12)	−37 (12)	−237 (8)	
H(103)	854 (13)	−24 (13)	−162 (8)	
H(121)	522 (13)	208 (13)	−139 (8)	
H(122)	608 (13)	307 (13)	−168 (8)	
H(123)	525 (12)	252 (13)	−222 (8)	
H(O2)	821 (13)	207 (13)	−463 (8)	
H(O5)	733 (12)	−185 (12)	−690 (8)	

Description and discussion

The geometry of the molecule and the labelling of atoms are displayed in Fig. 1. Bond distances and valence angles are listed in Table 2. Bonds involving H atoms do not show geometric anomalies and bond lengths range from 0·9 to 1·2 Å.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35521 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

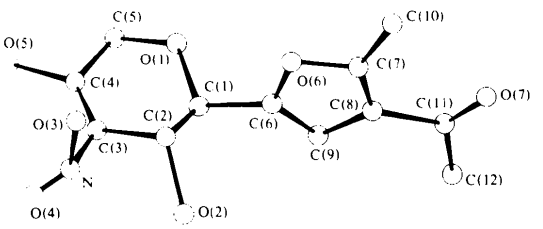

Fig. 1. Molecular conformation showing the atomic numbering.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)–C(2)	1·548 (13)	C(1)–C(6)	1·509 (11)
C(1)–O(1)	1·422 (11)	C(6)–C(9)	1·330 (13)
C(2)–C(3)	1·546 (10)	C(6)–O(6)	1·429 (12)
C(2)–O(2)	1·417 (10)	O(6)–C(7)	1·367 (11)
C(3)–N	1·509 (13)	C(7)–C(10)	1·526 (16)
N–O(3)	1·215 (12)	C(7)–C(8)	1·339 (16)
N–O(4)	1·218 (11)	C(8)–C(9)	1·493 (13)
C(3)–C(4)	1·524 (13)	C(8)–C(11)	1·492 (14)
C(4)–O(5)	1·443 (9)	C(11)–O(7)	1·208 (14)
C(4)–C(5)	1·556 (14)	C(11)–C(12)	1·498 (19)
C(5)–O(1)	1·440 (10)		

O(1)–C(1)–C(2)	109·8 (7)	O(1)–C(1)–C(6)	106·6 (7)
C(1)–C(2)–C(3)	107·8 (7)	C(2)–C(1)–C(6)	110·1 (7)
C(1)–C(2)–O(2)	111·5 (7)	C(1)–C(6)–O(6)	113·7 (7)
O(2)–C(2)–C(3)	105·7 (7)	C(1)–C(6)–C(9)	133·4 (9)
C(2)–C(3)–C(4)	112·1 (7)	C(6)–O(6)–C(7)	105·5 (7)
C(2)–C(3)–N	106·8 (7)	O(6)–C(7)–C(10)	115·3 (9)
C(3)–N–O(3)	118·4 (8)	O(6)–C(7)–C(8)	109·7 (9)
C(3)–N–O(4)	117·2 (8)	C(10)–C(7)–C(8)	134·9 (10)
O(3)–N–O(4)	124·4 (9)	C(7)–C(8)–C(9)	109·5 (9)
N–C(3)–C(4)	108·9 (7)	C(7)–C(8)–C(11)	123·8 (10)
C(3)–C(4)–O(5)	106·4 (7)	C(8)–C(11)–O(7)	121·6 (11)
O(5)–C(4)–C(5)	108·9 (8)	C(8)–C(11)–C(12)	114·9 (10)
C(3)–C(4)–C(5)	107·5 (8)	O(7)–C(11)–C(12)	123·5 (12)
C(4)–C(5)–O(1)	107·5 (8)	C(11)–C(8)–C(9)	126·7 (9)
C(5)–O(1)–C(1)	111·8 (7)	C(8)–C(9)–C(6)	102·9 (9)
		C(9)–C(6)–O(6)	112·9 (8)

The pyranose ring, as expected, is distorted from the ideal $^4C_1$ conformation by intramolecular interactions between substituent groups and by crystal-field effects. In terms of ring-puckering coordinates (Cremer & Pople, 1975), $q_2 = 0{\cdot}06$ (1) Å, $\varphi_2 = 323$ (1)° and $q_3 = 0{\cdot}6$ (1) Å. The puckering amplitudes describe a slightly distorted chair with $q_3 \gg q_2$. Indeed, the total puckering amplitude $Q = 0{\cdot}61$ Å lies only slightly under the Q value of an ideal cyclohexane chair [0·63 Å for R(C—C) = 1·54 Å]. The magnitude of the distortion is given by $\theta = 5{\cdot}4$ (9)°. The φ_2 value is close to 330° which corresponds to a twist-boat conformation. Because the pyranose chair is not a flexible ring (Dunitz & Waser, 1972) some bond lengths and valence angles must be different when the ring conformational angles are different. The C(1)—O(1) bond has the normal value and the C(1)—O(5) bond is in the usual range (1·43–1·44 Å). The values of the valence bond angles at the ring oxygen O(1) and at the anomeric carbon atom C(1) are characteristic of β-pyranose molecules. In α sugars these angles are 113·8 and 111·5°, respectively, whereas they are significantly less in β anomers, *i.e.* 112 and 107°. The O(1)—C(1)—C(6) valence angle is less than tetrahedral as in β-pyranoses.

The most important structural consequence of the anomeric effects is in the conformational angle of the glycosidic bond. The change in potential energy with rotation about the glycosidic bond calculated by *ab initio* quantum-mechanical methods (Jeffrey, Pople, Binkley & Vishveshwara, 1978) suggests that there are energy barriers of 8 to 20 kJ mol^{-1}. In consequence, the glycosidic torsion angles lie within quite narrow ranges for α- and β-pyranosides (Jeffrey & Tagaki, 1977). This anomeric conformational potential energy will also apply to other glycosidic-linkage bonds. The observed value for the O(1)—C(1)—C(6)—O(6) torsion angle of 54·3 (9) Å is near to the range 60–80° reported for methyl pyranosides (Jeffrey, Pople & Radom, 1972, 1974). The observed value for C(5)—O(1)—C(1)—C(6) is close to the theoretical value (180°) for the β configuration (shifts from this ideal value by 5° are reported since pyranose rings are not ideal $^4C_1$ chairs).

As shown by the torsion angles (Table 3) and least-squares planes (Table 4) all the substituent groups (furanose ring, NO_2 and OH groups) are equatorial as expected from steric considerations. The dihedral angle formed by the furanose ring plane and the pyranose mean plane of 95·8 (8)° indicates that the most important term in the conformational energy is the intramolecular potential energy.

The furyl ring is planar as shown in Table 4. In terms of ring puckering coordinates (Cremer & Pople, 1975) the amplitude phase magnitudes are $q = 0{\cdot}01$ (1) Å and $\varphi = 81$ (1)° but this amplitude of puckering, of the order of the standard deviations, is not significant.

An absolute-configuration determination was not

Table 3. *Torsion angles involving non-hydrogen atoms* (°)

(*a*) Six-membered ring	
C(4)—C(5)—O(1)—C(1)	67·8 (9)
C(2)—C(1)—O(1)—C(5)	−66·0 (9)
O(1)—C(1)—C(2)—C(3)	55·9 (9)
C(1)—C(2)—C(3)—C(4)	−53·2 (9)
C(2)—C(3)—C(4)—C(5)	55·9 (9)
C(3)—C(4)—C(5)—O(1)	−60·6 (9)
(*b*) Pyranose ring substituents	
C(6)—C(1)—C(2)—C(3)	173·0 (7)
C(6)—C(1)—O(1)—C(5)	174·7 (7)
O(2)—C(2)—C(3)—C(4)	−172·6 (7)
O(1)—C(1)—C(2)—O(2)	171·5 (6)
C(6)—C(1)—C(2)—O(2)	−71·3 (9)
O(2)—C(2)—C(3)—N	68·3 (8)
C(1)—C(2)—C(3)—N	−172·3 (7)
N—C(3)—C(4)—C(5)	173·8 (7)
N—C(3)—C(4)—O(5)	−69·7 (9)
C(2)—C(3)—N—O(3)	61·9 (10)
C(2)—C(3)—N—O(4)	−116·9 (9)
C(4)—C(3)—N—O(3)	−59·3 (10)
C(4)—C(3)—N—O(4)	121·9 (9)
C(2)—C(3)—C(4)—O(5)	172·4 (7)
O(5)—C(4)—C(5)—O(1)	−175·4 (7)
(*c*) Junction of the rings	
O(1)—C(1)—C(6)—O(6)	54·3 (9)
O(1)—C(1)—C(6)—C(9)	−126·7 (11)
C(2)—C(1)—C(6)—O(6)	−64·8 (9)
C(2)—C(1)—C(6)—C(9)	114·2 (11)
(*d*) Furyl ring substituents	
C(1)—C(6)—O(6)—C(7)	178·7 (8)
C(1)—C(6)—C(9)—C(8)	−178·1 (9)
C(10)—C(7)—O(6)—C(6)	176·3 (8)
C(10)—C(7)—C(8)—C(9)	−174·7 (10)
C(11)—C(8)—C(9)—C(6)	178·7 (9)
C(7)—C(8)—C(11)—C(12)	−178·4 (10)
C(9)—C(8)—C(11)—O(7)	−178·5 (10)

Table 4. *Least-squares planes*

Equations of the planes

I $\quad 0{\cdot}8092x - 0{\cdot}4789y + 0{\cdot}3403z = 3{\cdot}8559$

II $\quad -0{\cdot}6518x - 0{\cdot}7188y + 0{\cdot}2420z = -7{\cdot}3304$

Atomic deviations from the planes (Å)

	I		II
O(1)*	−0·174 (7)	O(6)*	−0·001 (8)
C(2)*	−0·215 (9)	C(6)*	0·004 (9)
C(3)*	0·194 (9)	C(7)*	−0·003 (12)
C(5)*	−0·355 (11)	C(8)*	0·005 (10)
C(1)*	0·316 (9)	C(9)*	−0·006 (11)
C(4)*	−0·244 (11)	C(10)	−0·098 (12)
O(2)	0·401 (6)	C(11)	0·026 (13)
O(5)	0·351 (8)	O(7)	0·060 (9)
N	−0·494 (8)	C(12)	−0·006 (15)
O(3)	−1·709 (8)	C(1)	0·039 (9)
O(4)	0·217 (9)	O(1)	−1·053 (7)
C(6)	−0·200 (9)	C(2)	1·371 (9)
O(6)	−1·619 (7)		
C(9)	0·389 (11)		

* Atoms included in the calculation of the least-squares plane.

Table 5. *Geometry of the hydrogen bonds*

	O–H (Å)	O···O (Å)	H···O (Å)	∠H–O···O (°)	∠O–H···O (°)
O(2)–H···O(7^{i})	0·9 (1)	2·75 (1)	1·9 (1)	13 (3)	160 (3)
O(5)–H···O(2^{ii})	1·0 (1)	2·92 (1)	2·0 (1)	17 (4)	154 (3)

Symmetry code

(i) $1-y, 1-x, -\frac{1}{2}-z$; (ii) $\frac{3}{2}-x, -\frac{1}{2}+y, -\frac{5}{4}-z$.

possible because of the low anomalous-dispersion corrections in the atomic scattering factors, but the configuration at the anomeric atom was fixed in the preparation reaction as shown by chemical methods of oxidative degradation (Asenjo-Asenjo, 1979) and, therefore, the reported configuration can be considered as the absolute configuration of the molecule in the crystal.

The geometry of some intermolecular contacts (Table 5) indicates hydrogen-bond character. The packing of the structure (Fig. 2) can be described by a three-dimensional hydrogen-bonding scheme between the helical chains of molecules around the 4_3 axes. Each molecule is linked by two hydrogen bonds O(2)···O(7) and O(7)···O(2) to the molecule related by the binary axis along [110]. The O(2)···H–O(5) hydrogen bonds form infinite chains along [100]. No other intermolecular contacts significantly shorter than the sum of the respective van der Waals radii are detected.

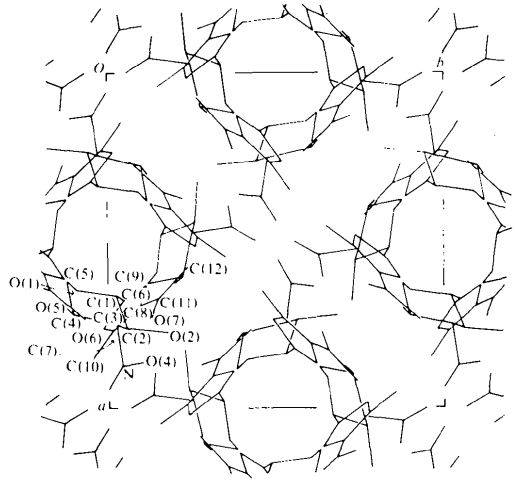

Fig. 2. The crystal structure viewed along the *c* axis.

The authors thank Professor J. López-Aparicio for suggesting the study and supplying the crystals. We also thank the X-ray Department of the Instituto Rocasolano, CSIC, and Dr F. H. Cano for collecting the diffractometric data and Professor A. López Castro for reading the manuscript and for valuable discussions. The present work is part of a wider research project supported by the Government through the Comisión Asesora de Investigación Científica y Técnica.

References

ASENJO-ASENJO, R. (1979). PhD Thesis. Univ. of Granada.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

DUNITZ, J. D. & WASER, J. (1972). *J. Am. Chem. Soc.* **94**, 5645–5650.

JEFFREY, G. A., POPLE, J. A., BINKLEY, S. & VISHVESHWARA, S. (1978). *J. Am. Chem. Soc.* **100**, 373–379.

JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1972). *Carbohydr. Res.* **25**, 117–131.

JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1974). *Carbohydr. Res.* **38**, 81–95.

JEFFREY, G. A. & TAGAKI, S. (1977). *Acta Cryst.* B**33**, 738–742.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. of York, England.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY system of crystallographic programs. Univ. of Maryland, College Park, Maryland, USA.