Calculations were carried out on a FACOM-M382 computer at the Data Processing Center, Kyoto University. The values for the molecular geometry were calculated using a part of the *KPPXRAY* (Taga, Higashi & Iizuka, 1985) program package.

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Structure of a Galacto-Benzofuranone Oxime

By M. J. Diánez, R. Vega, A. López-Castro and R. Márquez

Departamento de Optica y Sección de Física del Departamento de Investigaciones Físicas y Químicas del CSIC, Universidad de Sevilla, Spain

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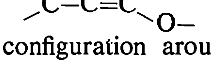
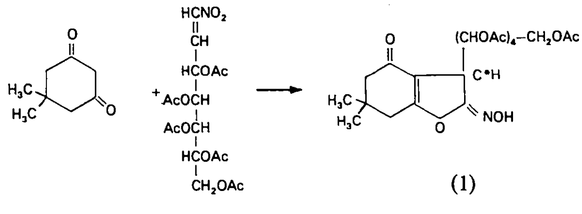
Abstract. (3*R*)-3,5,6,7-Tetrahydro-2-hydroxyimino-6,6-dimethyl-3-(1,2,3,4,5-penta-*O*-acetyl-D-*galacto*-pentitol-1-yl)benzofuran-4(2*H*)-one, $C_{25}H_{33}NO_{13}$, $M_r = 555·5$, orthorhombic, $P2_12_12_1$, $a = 11·105$ (1), $b = 30·316$ (2), $c = 8·436$ (1) Å, $V = 2840·0$ (4) Å^3, $Z = 4$, $D_m = 1·29$, $D_x = 1·30$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·0989$ mm^{-1}, $F(000) = 1176$, $T = 300$ K, final $R = 0·092$, $wR = 0·062$ for 1934 observed $[I > 2\sigma(I)]$ independent reflections. The form of the oxime is *E*. The cyclohexene ring conformation is 'half-chair' and the dihedral angle between the plane part of the cyclohexane ring and the furan plane is 7·1 (5)°. There is some electron delocalization along the resonance system  of the benzofuranone group. The configuration around the chiral centres of the sugar chain is *R*, *S*, *R* and *S* respectively, that is D-*galacto*. The new chiral centre C(3′) is *R*. Packing is governed by an intermolecular hydrogen bond between the oxime oxygen and the oxygen of the cyclohexenone group which stabilizes the crystal structure. No other intermolecular contacts significantly shorter than the sum of the van der Waals radii are observed.

Introduction. This compound is one of a series of benzofuran-4(5*H*)-one 'derivatives' that we are investigating in order to determine their stereochemistry in the solid state. We have previously reported the crystal structure of an analogue, the (3*R*)-3-(D-*galacto*-pentaacetoxypentyl-6,7-dihydro-2-hydroxyimino-4(5*H*)-benzofuranone (Diánez, López-Castro & Márquez, 1986). The title compound was obtained by an abnormal Michael reaction of 5,5-dimethylcyclohexane-1,3-dione with pentaacetoxy-1,2-dideoxy-1-nitrohept-1-enitol (Gómez-Sánchez, Galán, Rico & Bellanato, 1985).



(1)

These compounds are substances of considerable interest as precursors of *C*-glycosyl benzofuranones. A new chiral centre is produced (marked with an asterisk) and only an X-ray crystallographic study can help us to establish the crystal and molecular structure and the stereochemistry of this compound.

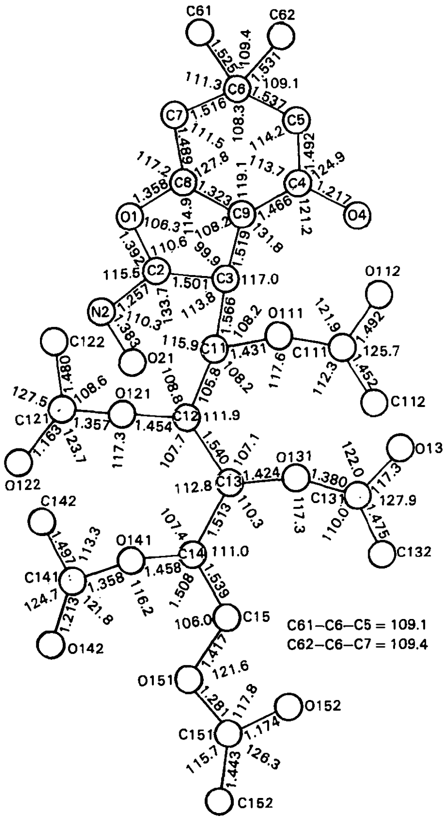
Experimental. Crystals are colourless prisms with well shaped faces (0·48 × 0·25 × 0·40 mm). D_m measured by flotation. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, lattice parameters from 25 reflections with $4 < \theta < 13°$. 4635 independent reflections ($0 \le h \le 15$, $0 \le k \le 42$, $0 \le l \le 11$) with $\theta \le 30°$. Two standard reflections (170 and $\bar{1}\bar{7}0$) monitored every 100 reflections showed only statistical fluctuations. 1934 reflections considered as observed [$I > 2\sigma(I_o)$], Lp corrections, but absorption and extinction corrections ignored. The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares on F with anisotropic thermal parameters for all non-H atoms ($w = 1/\sigma^2$). All H atoms localized on difference Fourier map and refined isotropically. Further least squares including positional parameters of the H atoms produced convergence with $R = 0{\cdot}092$, $wR = 0{\cdot}062$ and $S = 2{\cdot}12$. Final difference Fourier synthesis showed $|\Delta\rho| \le 0{\cdot}4\ \text{e Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1962). $(\Delta/\sigma)_{\max} = 2{\cdot}3$. The high R and $(\Delta/\sigma)_{\max}$ values are due to poor crystal quality. The absolute configuration was assumed on the basis of the compound used in the synthesis. The *XRAY* system (Stewart, Kundell & Baldwin, 1970) was used.

Discussion. The positional and isotropic thermal parameters for non-H atoms are given in Table 1.* Fig. 1 shows a schematic view of the molecule with the atom numbering, bond distances and angles. The values for the C(2)—N(2) and N(2)—O(2) bond lengths of 1·257 (13) and 1·382 (11) Å are in agreement with those reported previously (Jones & Chaney, 1972; Diánez, López-Castro & Márquez, 1986), and also compare well with the values ranging from 1·22 (3) to 1·33 (1) and 1·357 (18) to 1·439 (39) Å for the same bonds in other oximes (Ansell, Moore & Nielsen, 1971). This study reveals an oxime structure. The torsion angles O(21)—N(2)—C(2)—C(3) = −0·3 (14) and O(21)—N(2)—C(2)—O(1) = 179·2 (7)° show that the oxime group has an E conformation. The distribution of bond lengths indicates some electron delocalization in the fragment O(4), C(4), C(9), C(8), C(7) and O(1).

Table 1. *Fractional atomic parameters* ($\times 10^4$) *and* U_{eq} ($\text{Å}^2 \times 10^3$) *for the non-hydrogen atoms*

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}
O(1)	11390 (6)	3369 (3)	11542 (8)	56 (3)
N(2)	10348 (8)	3053 (3)	13517 (10)	57 (3)
C(2)	10366 (8)	3147 (3)	12066 (11)	47 (3)
O(21)	9286 (7)	2840 (2)	13900 (8)	61 (3)
C(3)	9502 (8)	3075 (3)	10723 (9)	36 (2)
C(4)	9991 (8)	3313 (3)	7675 (11)	42 (3)
O(4)	9235 (6)	3081 (2)	7045 (7)	55 (2)
C(5)	10837 (9)	3611 (3)	6815 (12)	56 (3)
C(6)	12159 (10)	3565 (4)	7326 (14)	63 (4)
C(7)	12238 (9)	3654 (4)	9090 (14)	64 (4)
C(8)	11230 (9)	3441 (4)	9967 (11)	49 (3)
C(9)	10193 (8)	3297 (3)	9390 (10)	40 (3)
C(11)	8198 (7)	3248 (3)	11064 (9)	36 (2)
C(12)	8115 (8)	3668 (3)	12016 (10)	36 (2)
C(13)	6808 (7)	3835 (3)	12151 (10)	39 (2)
C(14)	6700 (9)	4248 (3)	13146 (11)	44 (3)
C(15)	5381 (9)	4400 (3)	13263 (12)	52 (3)
C(61)	12923 (12)	3891 (5)	6385 (18)	96 (6)
C(62)	12586 (11)	3094 (4)	6983 (16)	79 (5)
O(111)	7606 (5)	3317 (2)	9579 (6)	39 (2)
O(112)	6929 (8)	2623 (2)	9589 (10)	76 (3)
C(111)	6984 (9)	2973 (3)	8946 (12)	52 (3)
C(112)	6403 (10)	3088 (4)	7460 (14)	64 (4)
O(121)	8817 (5)	4008 (2)	11227 (7)	39 (2)
O(122)	9709 (8)	4196 (3)	13489 (10)	76 (3)
C(121)	9596 (9)	4244 (3)	12129 (12)	49 (3)
C(122)	10237 (10)	4562 (3)	11098 (15)	68 (4)
O(131)	6117 (5)	3487 (2)	12828 (8)	45 (2)
O(132)	4903 (7)	3476 (3)	10715 (11)	91 (4)
C(131)	5150 (9)	3332 (4)	11964 (13)	58 (4)
C(132)	4507 (12)	2989 (4)	12869 (20)	94 (6)
O(141)	7061 (6)	4134 (2)	14756 (8)	50 (2)
O(142)	7462 (10)	4850 (2)	15203 (11)	88 (4)
C(141)	7466 (10)	4472 (3)	15670 (13)	58 (4)
C(142)	7840 (13)	4330 (4)	17297 (14)	76 (5)
O(151)	5048 (7)	4535 (2)	11716 (9)	63 (3)
O(152)	3533 (11)	4877 (6)	12567 (15)	253 (9)
C(151)	4107 (12)	4769 (4)	11466 (16)	81 (5)
C(152)	3877 (13)	4882 (4)	9832 (16)	88 (5)



C61–C6–C5 = 109.1
C62–C6–C7 = 109.4

Fig. 1. View of the molecule with atom numbering, bond lengths (Å) and angles (°); e.s.d.'s are 0·009–0·017 Å and 0·6–1·2°.

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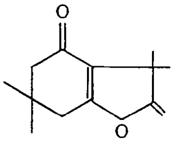
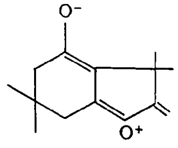
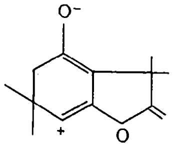
* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43712 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

From these observations, several canonical formulas are possible and dominant forms are as follows:


(I)


(II)


(III)

All lengths and angles in other moieties appear to be normal. The sugar chain C(11)—C(12)—C(13)—C(14)—C(15) is nearly planar [maximum deviation from the mean plane 0·019 (8) Å]. The five acetoxy groups are roughly planar [maximum deviation 0·016 (11) Å]. The torsion angles defining the orientation of the acetoxy groups with respect to the sugar chain are: C(13)—C(14)—O(141)—C(141) = 155·7 (7), C(14)—C(13)—O(131)—C(131) = 115·1 (3), C(13)—C(12)—O(121)—C(121) = 106·8 (8), C(12)—C(11)—O(111)—C(111) = −143·9 (7)°.

Fig. 2 shows the Newman projections corresponding to the C—C bonds of the sugar chain. The configurations around the chiral centres C(14), C(13), C(12) and C(11) are *R*, *S*, *R* and *S* respectively, in accordance with the D-*galacto* constitution. The new chiral centre C(3) is *R* (Klyne & Prelog, 1960).

The five-membered furan ring is nearly planar with each atom deviating $<0·011\,(11)$ Å from the best plane. The C(11) atom is out of the plane by 1·145 (8) Å and N(2) is at −0·022 (9) Å. C(4), C(9), C(8) and C(7) lie approximately in a plane [maximum deviation 0·022 (11) Å], and the angle between this plane and that of the five-membered ring is 6·2 (5)°. The cyclohexene ring conformation is half-chair. Cremer & Pople's (1975) puckering parameters for the sequence C(4)—C(5)—C(6)—C(7)—C(8)—C(9) are $\theta = 144\,(1)$, $\psi = -87\,(2)°$, $q_2 = 0·32\,(1)$, $q_3 = -0·31\,(1)$, $Q = 0·45\,(1)$ Å; the asymmetry parameters of Nardelli (1983) are $\Delta C_s[\mathrm{C}(6)] = 0·109\,(5)$ and $\Delta C_2[\mathrm{C}(6)\text{—}\mathrm{C}(5)] = 0·006\,(4)$.

The intermolecular packing arrangement showed only a hydrogen bond O(21)—H···O(4) (x, y, $z+1$) = 2·752 (9), O(21)—H = 1·05 (7), H···O(4) = 1·93 (7) Å, O(21)—H···O(4) = 137°. No other contacts less than the sums of the van der Waals radii are observed.

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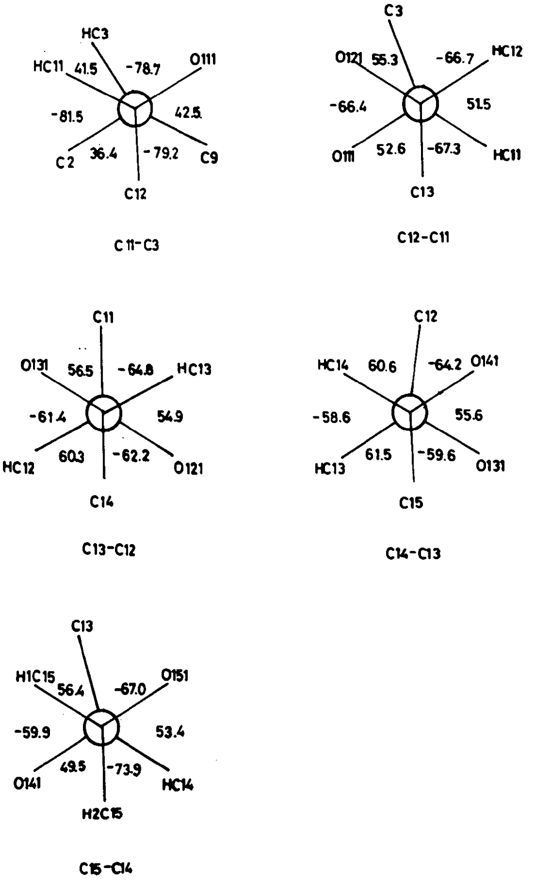

Fig. 2. Some Newman projections. Torsion angles in °; e.s.d.'s are in the range 0·6–1·7° (excluding those involving H atoms).

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