acid-dimer H bonds and the symmetry code is that given in Table 3. In this way these H bonds constitute a closely packed interwoven structure parallel to the *bc* plane, whereas the interactions in the **a** direction only involve the peripheral non-polar part of the molecule. Here, only one short intermolecular contact, of 2·76 (5) Å, between C(4) of the benzene ring and H(7) at $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ is worth mentioning.

All C···C contacts are larger than 3·40 Å.

References

Benedetti, E. (1982). *Chemistry and Biochemistry of Amino Acids, Peptides and Proteins*, edited by B. Weinstein, Vol. 6, pp. 105–184. New York: Marcel Dekker.

Domiano, P., Musatti, A., Pelizzi, C. & Predieri, G. (1974). *Cryst. Struct. Commun.* **3**, 531–534.

Frömming, K. H. & Vollenberg, W. (1966). *Arch. Pharm. (Weinheim, Ger.)*, **299**, 179–188.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Marsh, R. E. & Donohue, J. (1967). *Adv. Protein Chem.* **22**, 235–256.

Sheldrick, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

Spek, A. L. (1982). The *EUCLID* package. In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Acta Cryst. (1985). C**41**, 274–277

Structure of 5-*β*-D-Galactopyranosyl-1,3-dimethylbarbituric Acid Monohydrate,* $C_{12}H_{18}N_2O_8.H_2O$

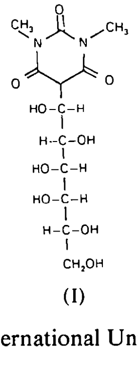
By M. Millan, C. F. Conde, A. Conde and R. Márquez

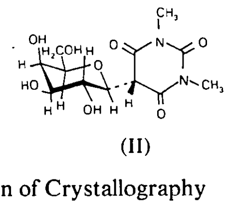
Departamento de Optica y Sección de Física del Centro Coordinado del CSIC, Universidad de Sevilla, Spain

(*Received* 27 *June* 1984; *accepted* 15 *October* 1984)

Abstract. $M_r = 336·30$, orthorhombic, $P2_12_12_1$, $a = 9·147\ (1)$, $b = 23·054\ (2)$, $c = 6·921\ (1)$ Å, $V = 1459·5\ (3)$ Å^3, $Z = 4$, $D_m = 1·53\ (1)$, $D_x = 1·531$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 0·12$ mm^{-1}, $F(000) = 712$, $T = 300$ K, $R = 0·055$ for 1623 observed independent reflexions. The galactopyranose ring adopts a $^4C_1$ conformation and the dihedral angle between the two rings in the molecule is 89·1 (1)°. The molecules are linked by an extensive three-dimensional hydrogen-bond network involving the water hydration molecule which stabilizes the crystal structure.

Introduction. The structure determination of the title compound was undertaken as part of a continuing project on conformational details of *C*-nucleosides in the solid state. In this connexion some imidazole *C*-nucleosides have been studied (Criado, Conde & Márquez, 1983, 1984, for example). The discovery of *C*-nucleosides and their pharmacological properties has directed considerable attention to the development of synthetic routes to this class of compounds. Many ways to prepare them are known, but they are generally very laborious and require the convenient protection and functionalization of the sugar precursor. Recently, an easy synthesis of *C*-nucleoside derivatives of barbituric acids by reaction of aldoses with the barbituric acid (or its 1,3-dimethyl derivative) has been reported (Avalos González, 1981; Galbis Pérez, Avalos González, Jiménez Requejo & Palacios Albarrán, 1983). In this way, the reaction of 1,3-dimethylbarbituric acid with D-galactose yields the acyclic *C*-glycoside (I) or its cyclic analogue (II) by dehydration of the sugar side chain. After acetylation, the cyclic form was established for the tetra-*O*-acetyl derivative from spectral data (UV, IR and ^{1}H NMR). For the non-acetylated compound the acyclic form was initially proposed and an X-ray analysis was suggested to elucidate the molecular form and, finally, the cyclic *C*-nucleoside structure was established.


(I)


(II)

---

* Barbituric acid is 2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione.

0108-2701/85/020274-04$01.50

Experimental. Crystals of the title compound, prepared as previously described in the Organic Chemistry Department of the University of Extremadura, were kindly supplied by Professor J. Galbis. Colourless crystals in the form of prisms elongated along [001]. D_m by flotation method. Crystal 0·15 × 0·20 × 0·45 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Cell dimensions obtained from 25 reflexions in the range $3 < \theta < 16°$. Total of 2466 independent reflexions ($0 \leq h \leq 12$, $0 \leq k \leq 32$, $0 \leq l \leq 9$) measured in the range $2 \leq \theta \leq 30°$, ω–2θ scan technique. Two standards ($2\bar{7}1$, $27\bar{1}$), variation in intensity less than 3% for mean values. 843 reflexions considered unobserved [$I < 2\sigma(I)$]. No correction for absorption or extinction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The absolute configuration was assumed on the basis of the configurations of the compounds used in the synthesis. Full-matrix least-squares refinement; $\sum w(|F_o| - |F_c|)^2$ minimized with weighting scheme based on the statistical count criterion ($w = 1/\sigma^2$). Difference Fourier synthesis revealed the 20 H-atom positions; isotropic temperature factor $U = 0{\cdot}037$ Å^2 for H atoms. Further least squares including positional parameters of the H atoms. At final convergence $\Delta/\sigma < 0{\cdot}07$, $R = 0{\cdot}055$, $R_w = 0{\cdot}056$, $S = 1{\cdot}88$ for 269 refined variables. Max. and min. values in final difference density map 0·30 and $-0{\cdot}25$ e Å^{-3}, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations carried out on a Univac 1100 computer. Crystallographic programs of the *XRAY*70 system (Stewart, Kundell & Baldwin, 1970) used throughout.

Discussion. Fractional atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) for non-hydrogen atoms are given in Table 1.* Bond lengths and angles involving non-hydrogen atoms are listed in Fig. 1. For bonds involving H atoms C—H distances range from 0·83 (6) to 1·06 (7) Å [mean value 0·96 (6) Å] and O—H bond lengths from 0·81 (6) to 0·87 (6) Å [mean value 0·83 (6) Å].

In the galactopyranose ring the mean values for the C—C and C—O bond lengths are 1·532 (6) and 1·431 (6) Å, respectively, in agreement with the mean values of 1·522 (2) and 1·426 (2) Å obtained from 57 pyran compounds (Ohanessian, Longchambon & Arene, 1978) and the mean value of the endocyclic angles at the C atoms is 110·4 (3)°, in agreement with sp^3 hybridization of the C atoms. The angles O(4)—C(11)—C(12) and C(10)—C(11)—C(12) show a difference of 5·1 (6)°; this difference is in the range 5–9° reported for oligosaccharides. This angular distortion is due to interactions between the substituents at C(10) and C(11).

The galactopyranose ring adopts the $^4C_1$ conformation as in most D-pyranoses. In terms of ring-puckering coordinates (Cremer & Pople, 1975), the values of the amplitude–phase pair (q_2,φ_2) and puckering coordinate q_3 are 0·089 (4) Å, −34 (3)° and 0·568 (4) Å [$Q = 0{\cdot}575$ (4) Å and $\theta = 8{\cdot}9$ (4)°] for the sequence O(4)—C(7)—C(8)—C(9)—C(10)—C(11). The

Table 1. *Atomic fractional coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	6660 (5)	5480 (2)	3216 (8)	30 (1)
C(2)	7307 (5)	6128 (2)	525 (7)	25 (1)
C(3)	6028 (5)	5908 (2)	−605 (7)	24 (1)
C(4)	5243 (6)	5393 (2)	219 (8)	31 (2)
C(5)	4802 (7)	4729 (3)	2929 (11)	51 (2)
C(6)	8545 (7)	6222 (3)	3664 (9)	46 (2)
C(7)	5005 (5)	6435 (2)	−919 (7)	21 (1)
C(8)	3728 (5)	6327 (2)	−2314 (7)	23 (1)
C(9)	2680 (5)	6847 (2)	−2301 (7)	24 (1)
C(10)	2284 (5)	7049 (2)	−258 (7)	25 (1)
C(11)	3696 (5)	7134 (2)	878 (7)	22 (1)
C(12)	3411 (5)	7316 (2)	2960 (7)	27 (1)
N(1)	5562 (5)	5237 (2)	2101 (7)	30 (1)
N(2)	7429 (5)	5945 (2)	2423 (6)	30 (1)
O(1)	6960 (5)	5297 (2)	4800 (6)	44 (1)
O(2)	8170 (4)	6476 (2)	−159 (6)	37 (1)
O(3)	4373 (5)	5118 (2)	−733 (7)	46 (1)
O(4)	4491 (3)	6595 (1)	945 (5)	23 (1)
O(5)	4742 (4)	7351 (1)	4038 (5)	33 (1)
O(6)	1382 (4)	6641 (2)	713 (6)	35 (1)
O(7)	1397 (4)	6674 (2)	−3313 (6)	35 (1)
O(8)	4378 (4)	6259 (1)	−4186 (5)	30 (1)
O(9)	2588 (4)	5756 (2)	3227 (6)	39 (1)

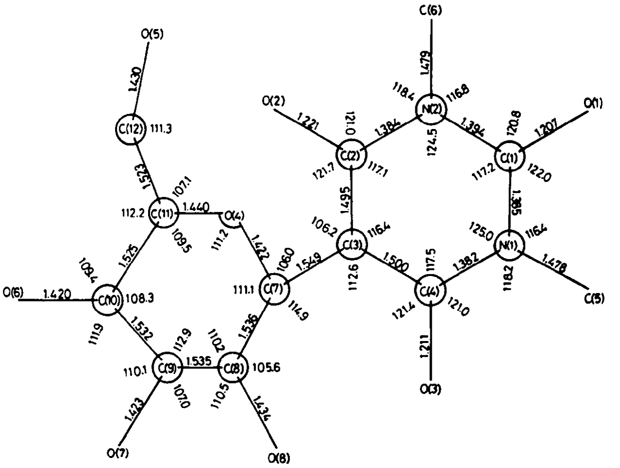


Fig. 1. Bond lengths (Å) and angles (°) in the molecule. (Standard deviations are in the ranges 0·006–0·008 Å and 0·3–0·5°, respectively.)

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39836 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

asymmetry parameter of Nardelli (1983) is ΔC_2[O(4)—C(11)] = 0·002 (3). The mean value of the endocyclic torsion angles is 56·7 (4)° [values range from 47·5 (5) to 67·1 (4)° in agreement with the calculated mean value (57·4°) for galactosyl derivatives (Longchambon, Ohanessian, Avenel & Newman, 1975)].

The torsion angles C(10)—C(11)—C(12)—O(5) 175·6 (4) and O(4)—C(11)—C(12)—O(5) 55·4 (5)° indicate a *trans–gauche* conformation for the exocyclic bond. This conformation is the most frequent: 71% for 17 galactopyranosyl compounds (*gg*: 12%, *gt*: 17%) (Longchambon, Ohanessian & Gillier-Pandraud, 1981). In the barbituric acid moiety the mean values for the endocyclic N—C and C—C bond lengths are 1·386 (5) and 1·498 (6) Å, respectively, in agreement with those reported for barbituric acid derivatives (Craven, Vizzini & Rodrigues, 1969; Shimizu, Nishigaki, Nakai & Osaki, 1982). The ring adopts a twist–boat conformation, as described by the puckering coordinates (Cremer & Pople, 1975): q_2 = 0·070 (5) Å, φ_2 = 144 (4)° and q_3 = 0·098 (5) Å [Q = 0·120 (5) Å, θ = 35 (2)°] for the sequence C(1)—N(2)—C(2)—C(3)—C(4)—N(1). The asymmetry parameter of Nardelli (1983) is ΔC_2[C(1)—N(1)] = 0·004 (2). The O(2) and O(3) atoms deviate by 0·238 (4) and 0·176 (4) Å, respectively, from the least-squares plane through the ring. The dihedral angle between the two rings in the molecule is 89·1 (1)°.

Crystal packing

Fig. 2. shows a view along [100] of a molecule with its neighbours in the crystal. The crystal structure is stabilized by a three-dimensional hydrogen-bonding network. Each molecule is linked to two neighbours by O(5)—H(O5)···O(8)($x,y,z+1$) and C(12)—H(121)···O(7)($x,y,z+1$) and C(9)—H(9)···O(5)($x,y,z-1$) to form chains parallel to [001]. On the other hand, the molecules are linked by an O(6)—H(O6)···O(2)($x-1,y,z$) interaction to form double chains parallel to [100] in which each molecule is also linked by O(7)—H(O7)···O(5)($x-\frac{1}{2},\frac{3}{2}-y,-z$) to the neighbour related by a twofold screw axis along the a axis. Finally, the water molecule is involved in three hydrogen bonds [O(8)—H(O8)···O(9)($x,y,z-1$), O(9)—H(O91)···O(3)($-x+\frac{1}{2},-y+1,z+\frac{1}{2}$) and O(9)—H(O92)···O(6)(x,y,z)] with three neighbouring molecules. Details of the geometry of these hydrogen bonds are given in Table 2.

Table 2. *Geometry of the possible hydrogen bonds*

X—H···Y	X···Y	H···Y	X—H	∠X—H···Y
O(5)—H(O5)···O(8^{i})	2·821 (5) Å	2·06 (6) Å	0·87 (6) Å	146 (6)°
O(6)—H(O6)···O(2^{ii})	3·024 (5)	2·25 (7)	0·82 (7)	158 (6)
O(7)—H(O7)···O(5^{iii})	2·756 (5)	1·93 (7)	0·83 (7)	177 (7)
O(8)—H(O8)···O(9^{iv})	2·690 (5)	1·89 (7)	0·81 (7)	165 (7)
O(9)—H(O91)···O(3^{v})	2·792 (5)	1·88 (7)	0·92 (7)	170 (7)
O(9)—H(O92)···O(6)	2·900 (5)	2·08 (7)	0·82 (7)	174 (7)
C(8)—H(8)···O(3)	3·052 (6)	2·36 (6)	1·05 (6)	122 (4)
C(9)—H(9)···O(5^{iv})	3·365 (6)	2·55 (7)	0·98 (6)	140 (5)
C(12)—H(121)···O(7^{i})	3·498 (6)	2·60 (7)	0·97 (7)	154 (5)

Symmetry code: none x, y, z; (i) $x, y, z+1$; (ii) $x-1, y, z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, -z$; (iv) $x, y, z-1$; (v) $-x+\frac{1}{2}, -y+1, z+\frac{1}{2}$.

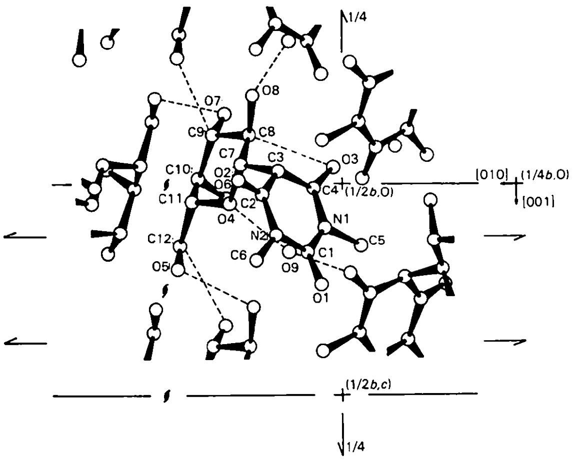


Fig. 2. A view of the asymmetric unit with its surroundings. Hydrogen bonds are indicated by dashed lines.

For the O—H···O contacts listed in Table 2 the values of the d parameter, defined as the difference between the sum of the van der Waals radii and the interatomic distance H···O (Taylor & Kennard, 1982), range between 0·45 and 0·82 Å; in all cases it is significantly higher than 0·3 Å and the O—H···O angles agree with the mean value reported [165·8 (12)°] for bonds with O···H < 1·812 Å (Allen, Kennard & Taylor, 1983), except for O(5)—H(5)···O(8) = 146 (6)° which is significantly smaller. For the C—H···O interactions the value of the d parameter is also higher than 0·3 Å and the angles C—H···O, ranging between 122 (4) and 154 (5)°, are above the limit of 90° (Allen, Kennard & Taylor, 1983) and so should be considered as hydrogen bonds.

We wish to thank Professor J. A. Galbis for supplying the crystals and for helpful discussions on chemical aspects and Professor A. López-Castro for collecting the diffraction data. The present work is part of a project supported by a grant from the Comisión Asesora de Investigación Científica y Técnica of the Spanish Government.

References

ALLEN, F. H., KENNARD, O. & TAYLOR, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

AVALOS GONZÁLEZ, M. (1981). Doctoral Thesis. Univ. of Extremadura, Spain.

CRAVEN, B. M., VIZZINI, E. A. & RODRIGUES, M. M. (1969). *Acta Cryst.* **B25**, 1978–1993.

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

CRIADO, A., CONDE, A. & MÁRQUEZ, R. (1983). *Acta Cryst.* C**39**, 122–125.

CRIADO, A., CONDE, A. & MÁRQUEZ, R. (1984). *Acta Cryst.* C**40**, 188–190.

GALBIS PÉREZ, J. A., AVALOS GONZÁLEZ, M., JIMÉNEZ REQUEJO, J. L. & PALACIOS ALBARRÁN, J. C. (1983). *Carbohydr. Res.* **124**, C15–C17.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LONGCHAMBON, F., OHANESSIAN, J., AVENEL, D. & NEWMAN, A. (1975). *Acta Cryst.* B**31**, 2623–2627.

LONGCHAMBON, F., OHANESSIAN, J. & GILLIER-PANDRAUD, H. (1981). *Acta Cryst.* B**37**, 601–607.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, P., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

NARDELLI, M. (1983). *Acta Cryst.* C**39**, 1141–1142.

OHANESSIAN, J., LONGCHAMBON, F. & ARENE, C. (1978). *Acta Cryst.* B**34**, 3666–3671.

SHIMIZU, N., NISHIGAKI, S., NAKAI, Y. & OSAKI, K. (1982). *Acta Cryst.* B**38**, 2309–2311.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The *XRAY70* system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Acta Cryst. (1985). C**41**, 277–280

Structure and Absolute Configuration of 1'-(*p*-Bromophenyl)-3'-ethyl-1',3',4',5'-tetrahydro-1,2-dideoxy-α-L-glucofuranoso[2,1-*d*]imidazole-2'-thione Monohydrate,* $C_{15}H_{19}BrN_2O_4S.H_2O$

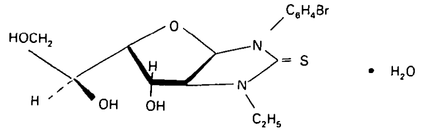
BY C. F. CONDE, M. MILLAN, A. CONDE AND R. MÁRQUEZ

Departamento de Optica y Sección de Física del Centro Coordinado del CSIC, Universidad de Sevilla, Spain

(*Received* 27 *June* 1984; *accepted* 15 *October* 1984)

Abstract. $M_r = 421{\cdot}30$, monoclinic, $P2_1$, $a = 7{\cdot}531$ (1), $b = 8{\cdot}148$ (4), $c = 14{\cdot}625$ (2) Å, $\beta = 97{\cdot}14$ (1)°, $V = 890{\cdot}5$ (5) Å^3, $Z = 2$, $D_m = 1{\cdot}58$ (1), $D_x = 1{\cdot}571$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 2{\cdot}42$ mm^{-1}, $F(000) = 432$, $T = 300$ K, $R = 0{\cdot}065$ for 1672 observed independent reflexions. The sugar ring adopts a $^4T_3$ conformation and the dihedral angle in the bicyclic system is 72·3 (4)°. A three-dimensional network of hydrogen bonds links the molecules to build up the crystal structure.

Introduction. The structure determination of the title compound (I) was undertaken as part of a continuing research project in this laboratory involving glucimidazoles and imidazole *C*-nucleosides. During the past few years amino-sugars have been used in the preparation of these compounds (Garcia González, Fernández-Bolaños & Lopez-Aparicio, 1976; Fernández-Bolaños, Galbis Pérez & Zamora Mata, 1984; Galbis Pérez, Palacios Albarrán, Jiménez Requejo & Avalos González, 1984) *via* l-arylglucofuranosoimidazolidine-2-thiones. Some of these compounds, prepared in the Organic Chemistry Department of the University of Extremadura, have been studied in order to establish the conformational details of the molecule in the solid state (for example, Estrada, Conde & Márquez, 1983, 1984). Galbis Pérez *et al.* (1984) have reported the application of aminonitrile synthesis to the preparation of the new 2-deoxy-2-(ethylamino)-α-L-glucopyranose hydrochloride and its reaction with 4-bromophenyl isothiocyanate, to afford the title compound. Its chemical nature was established from elemental analysis and spectroscopic IR and NMR data and the X-ray analysis was carried out to define the structural details.



(I)

Experimental. Single crystals in the form of colourless needles elongated along [100] prepared in the Organic Chemistry Department of the University of Extremadura and kindly supplied by Professor J. A. Galbis. D_m by flotation method. Crystal 0·09 × 0·14 × 0·30 mm. Unit-cell parameters by least squares from 25 reflexions, $5 < \theta < 18°$. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, $2\theta < 60°$ $(-10 \le h \le 10,\ 0 \le k \le 11,\ 0 \le l \le 20)$, ω–2θ scan

---

* IUPAC name: 6-(*p*-bromophenyl)-2-(1,2-dihydroxyethyl)-4-ethyl-3-hydroxy-2,3,3a,5,6,6a-hexahydrofuro[2,3-*d*]imidazole-5(4*H*)-thione monohydrate.