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p-Nitrophenyl α-D-Mannopyranoside Hemihydrate

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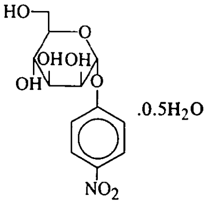
Abstract

In the title compound, $2C_{12}H_{15}NO_8.H_2O$, the pyranoside rings deviate slightly from an ideal chair conformation and the Ci05—Oi05—Ci01—Oi01—Ci07 (i = 1, 2) moieties display *gauche–gauche* conformations. The water molecule links two independent molecules in the asymmetric unit through O—H···O hydrogen bonds. All the hydroxy groups are involved in hydrogen-bond interactions giving rise to a three-dimensional network.

Comment

The molecular structure determination of the title compound, (I), was undertaken as part of a program of study of carbohydrate–carbohydrate interactions using glycophanes as models and α and β derivatives of glucose, galactose and mannose (Coteron, Vicent, Bosso & Penades, 1993).



(I)

The absolute configuration of the title molecule was not determined since it was known from the synthesis and was assigned according to the configurational angles given by Cano *et al.* (1985). The molecular structures of both independent molecules (hereafter i = 1 and 2, *e.g.* Ci03 is C103 when i = 1 and C203 when i = 2) have been compared by means of half-normal probability plots (Abrahams & Keve, 1971). The main differences are those concerning the exocyclic Ci03—Ci04—Oi04 angles and the disposition of the phenyl rings with respect to the pyranose ring. These differences can be attributed to steric effects and are evident in the fact that the smaller the Ci03—Ci04—Oi04 angle the greater the Oi04—Ci04—Ci05—Ci06 torsion angle [112.1 (5) and 60.4 (6), and 105.4 (4) and 73.6 (5)° for i = 1 and 2, respectively]. The phenyl ring of molecule (1) (i = 1) appears to be more coplanar with the anomeric Ci01 atom than that of molecule (2) (i = 2) giving rise to distorsions in the disposition of the Oi01 atom [Ci03—Ci02—Ci01—Oi01 −69.4 (6) and −62.0 (5), and Ci01—Oi01—Ci07—Ci08 11.4 (8) and 38.3 (8)°, for i = 1 and 2, respectively].

The pyranose rings show slightly distorted chair conformations as measured by the Cremer & Pople (1975) parameters [molecule (1): Q = 0.556 (5), θ = 4.9 (5), φ = 144 (7); molecule (2): Q = 0.561 (4), θ = 5.2 (5), φ = −40 (5)] analogous to the conformations of other mannose derivatives obtained from the Cambridge Structural Database (Allen *et al.*, 1991). Only 10 organic structures with $R < 0.10$, free of error and disorder, and without fused rings in order to avoid conformational distortions, were found, namely, ADISTM, ADMANN, ADMHEP, AMANOA, BIFTUF, COFMEP10, FABYOW10, JUKREM, MEMANP and MEMANP11.

The endocyclic Oi05—Ci05 and Oi05—Ci01 bond lengths (Table 2) are significantly different, with the shorter bond close to the anomeric C atom, analogous to previously reported *p*-nitropyranose compounds [BAXSEY (Swaminathan, 1982), BAXSEY01 (Jones, Sheldrick, Kirby & Cruse, 1982), NPBDXY (Harata, 1976) and NPGAMM (Brehm & Moult, 1975)]. The glycosidic Ci01—Oi01 bonds in molecules (1) and (2) are unequal, the larger bond being observed in molecule (1) where the phenyl ring is closer to the sugar moiety [Ci01—Oi01—Ci07—Ci08 11.4 (8) and 38.3 (8)° for i = 1 and 2]. Apart from the widening of the Ci08—Ci07—Oi01 external angle at the benzene ring [124.6 (6) and 124.5 (5)° for i = 1 and 2], which is also displayed by the *p*-nitropyranose molecules already mentioned, no significant differences in the glycosidic bond have been observed for the two independent molecules of the glucopyranoside derivatives BAXSEY and BAXSEY01. The glycosidic torsion angles of 59.6 (6) and 61.4 (6)° (Oi05—Ci01—Oi01—Ci07 for i = 1 and 2) are very close to the ideal value of 60°. The conformations of the primary alcohol groups are almost staggered showing Oi05—Ci05—Ci06—Oi06 torsion angles of up to −72.9 (5) and −71.6 (5)° for i = 1 and 2, respectively. The Ci01—Oi01—Ci07 bond angles [119.7 (5) and 119.1 (4)°, for i = 1 and 2] fall in the range reported for aryl pyranosides [117.3 (3)–120.4 (3)°; Swaminathan, 1982]. The nitro groups are almost coplanar with the phenyl rings, similar to the already mentioned analogous *p*-nitropyranose derivatives (Allen *et al.*, 1991). In the title compound, however, both N—O distances are not alike, the longest being involved in C—H hydrogen-bonding interactions.

The Oi01—Ci07 bond lengths of 1.356 (6) and 1.361 (6) Å for i = 1 and 2, respectively, are in agreement with the values reported (Allen *et al.*, 1987) for enol esters [1.354 (16) Å], showing a partial double-

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bond character that reflects the resonance of the glycosidic O-atom lone pairs with the aromatic ring. The water molecule links the two molecules, acting as donor and acceptor in an almost tetrahedral environment. There are eight O—H···O hydrogen bonds in which all OH groups, except for the O104 group, act as donors and acceptors. The crystal structure is composed of these units linked together in a rather complicated three-dimensional network. There are also two weak C—H···phenyl contacts (Table 3).

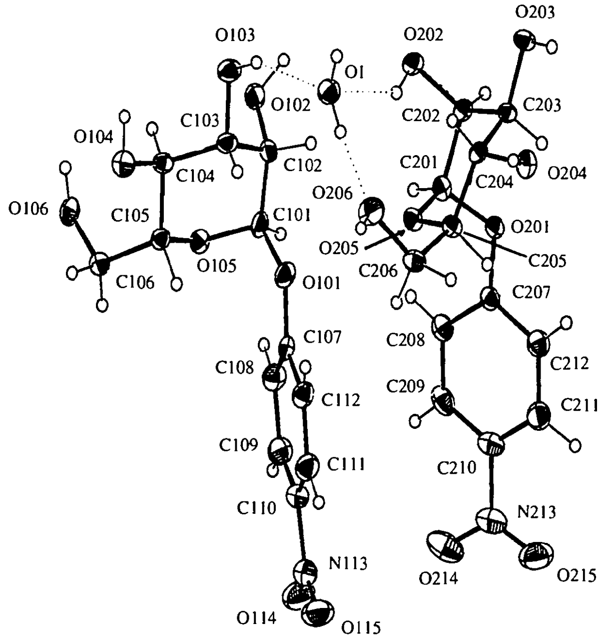

Fig. 1. The molecular structure and labelling scheme for (I). Atomic displacement ellipsoids are drawn at the 30% probability level.

In the crystal, the molecules pack in a compact manner without voids. The total packing coefficient is 0.71. This high value is reflected in the calculated density of 1.53 Mg m^{-3}.

Experimental

The title compound was obtained as a commercial sample from the Sigma Chemical Company.

Crystal data

$2C_{12}H_{15}NO_8.H_2O$
$M_r = 620.52$
Monoclinic
$P2_1$
$a = 17.797\ (3)$ Å
$b = 10.2594\ (6)$ Å
$c = 7.4438\ (5)$ Å
$\beta = 98.44\ (1)°$
$V = 1344.4\ (2)$ Å^3
$Z = 2$
$D_x = 1.533$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 58 reflections
$\theta = 2–45°$
$\mu = 1.14$ mm^{-1}
$T = 293$ K
Plate
0.33 × 0.20 × 0.07 mm
Colourless

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2720 measured reflections
2451 independent reflections
2451 observed reflections [F set to zero for negative F^2]

$R_{\rm int} = 0.024$
$\theta_{\rm max} = 67°$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 8$
2 standard reflections
frequency: 100 min
intensity decay: none

Refinement

Refinement on F
$R = 0.069$
$wR = 0.069$
$S = 1.017$
2451 reflections
387 parameters
H-atom parameters not refined
$w = 0.5551/\{[\chi(|F_o|)]^2 \times g(\sin\theta/\lambda)\}$
$(\Delta/\sigma)_{\rm max} = 0.013$

$\Delta\rho_{\rm max} = 0.253$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.211$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: $1.32\ (6) \times 10^4$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C101	0.2858 (3)	0.4807 (6)	0.7622 (7)	0.037 (3)
C102	0.3652 (3)	0.4317 (6)	0.8143 (7)	0.037 (3)
C103	0.3778 (3)	0.3869 (6)	1.0137 (7)	0.034 (2)
C104	0.3540 (3)	0.4929 (6)	1.1344 (7)	0.031 (2)
C105	0.2722 (3)	0.5319 (6)	1.0697 (6)	0.029 (2)
C106	0.2425 (3)	0.6405 (6)	1.1740 (7)	0.038 (3)
O101	0.2381 (2)	0.3675 (5)	0.7592 (5)	0.038 (2)
O102	0.4167 (2)	0.5342 (5)	0.7878 (5)	0.040 (2)
O103	0.4553 (2)	0.3557 (5)	1.0700 (6)	0.047 (2)
O104	0.3577 (2)	0.4508 (5)	1.3187 (5)	0.041 (2)
O105	0.2654 (2)	0.5752 (5)	0.8818 (4)	0.032 (2)
O106	0.2930 (2)	0.7490 (5)	1.1990 (5)	0.039 (2)
C107	0.1620 (3)	0.3794 (6)	0.7094 (6)	0.034 (2)
C108	0.1259 (3)	0.4906 (6)	0.6297 (9)	0.046 (3)
C109	0.0490 (3)	0.4893 (7)	0.5768 (8)	0.047 (3)
C110	0.0079 (3)	0.3784 (8)	0.6029 (8)	0.047 (3)
C111	0.0432 (3)	0.2698 (7)	0.6870 (8)	0.047 (3)
C112	0.1196 (3)	0.2702 (7)	0.7352 (7)	0.041 (3)
N113	−0.0734 (3)	0.3761 (7)	0.5416 (8)	0.057 (3)
O114	−0.1021 (3)	0.4732 (7)	0.4587 (8)	0.078 (3)
O115	−0.1101 (3)	0.2804 (7)	0.5729 (9)	0.079 (3)
C201	0.3348 (3)	0.1376 (6)	0.4528 (7)	0.031 (2)
C202	0.4171 (3)	0.0995 (6)	0.4489 (7)	0.032 (2)
C203	0.4217 (3)	−0.0494 (6)	0.4345 (6)	0.026 (2)
C204	0.3855 (3)	−0.1142 (6)	0.5869 (6)	0.028 (2)
C205	0.3066 (3)	−0.0616 (6)	0.5963 (7)	0.031 (2)
C206	0.2749 (3)	−0.1070 (6)	0.7633 (8)	0.037 (3)
O201	0.2945 (2)	0.0951 (5)	0.2848 (4)	0.033 (2)
O202	0.4651 (2)	0.1519 (5)	0.6023 (5)	0.035 (2)
O203	0.4987 (2)	−0.0882 (5)	0.4408 (5)	0.033 (2)
O204	0.3793 (2)	−0.2504 (5)	0.5398 (5)	0.037 (2)
O205	0.3074 (2)	0.08000	0.6012 (4)	0.032 (2)
O206	0.3280 (2)	−0.0858 (6)	0.9237 (5)	0.050 (2)
C207	0.2187 (3)	0.1198 (6)	0.2464 (7)	0.033 (2)

C208	0.1840 (3)	0.2346 (7)	0.2921 (8)	0.044 (3)
C209	0.1076 (3)	0.2513 (8)	0.2411 (8)	0.049 (3)
C210	0.0656 (3)	0.1558 (7)	0.1397 (8)	0.045 (3)
C211	0.0992 (3)	0.0425 (7)	0.0915 (8)	0.046 (3)
C212	0.1755 (3)	0.0243 (7)	0.1433 (8)	0.043 (3)
N213	−0.0156 (3)	0.1731 (8)	0.0845 (8)	0.058 (3)
O214	−0.0463 (3)	0.2672 (8)	0.1493 (9)	0.087 (4)
O215	−0.0501 (3)	0.0949 (8)	−0.0171 (8)	0.083 (3)
O1	0.4440 (2)	0.0937 (5)	0.9532 (5)	0.042 (2)

Table 2. *Selected geometric parameters (Å, °)*

C101—C102	1.496 (7)	C201—C202	1.520 (7)
C101—O101	1.437 (8)	C201—O201	1.416 (6)
C101—O105	1.400 (7)	C201—O205	1.401 (6)
C102—C103	1.538 (8)	C202—C203	1.534 (8)
C102—O102	1.427 (7)	C202—O202	1.428 (6)
C103—C104	1.510 (8)	C203—C204	1.536 (7)
C103—O103	1.418 (6)	C203—O203	1.421 (6)
C104—C105	1.518 (6)	C204—C205	1.516 (7)
C104—O104	1.430 (6)	C204—O204	1.440 (7)
C105—O105	1.455 (6)	C205—O205	1.453 (6)
C102—C101—O101	105.5 (5)	C202—C201—O201	105.6 (4)
C102—C101—O105	113.0 (4)	C202—C201—O205	110.7 (4)
O101—C101—O105	111.2 (4)	O201—C201—O205	112.1 (4)
C101—C102—C103	110.4 (4)	C201—C202—C203	108.6 (4)
C101—C102—O102	108.5 (5)	C201—C202—O202	110.7 (4)
C102—C103—C104	110.2 (5)	C202—C203—C204	110.3 (4)
C102—C103—O103	110.5 (4)	C202—C203—O203	109.7 (4)
C103—C104—C105	109.9 (4)	C203—C204—C205	111.8 (4)
C103—C104—O104	112.1 (5)	C203—C204—O204	105.4 (4)
C104—C105—O105	109.1 (4)	C204—C205—O205	110.5 (4)
C101—O105—C105	114.0 (4)	C201—O205—C205	113.9 (4)

O101—C101—O105—C105	61.0 (5)
C102—C101—O105—C105	−57.3 (6)
O102—C102—C101—O105	−68.9 (6)
C103—C102—C101—O105	52.2 (7)
O103—C103—C102—C101	−172.8 (5)
C104—C103—C102—C101	−51.8 (6)
O104—C104—C103—C102	174.3 (4)
C105—C104—C103—C102	55.6 (6)
C106—C105—C104—C103	−177.7 (5)
O105—C105—C104—C103	−57.9 (6)
O201—C201—O205—C205	55.1 (5)
C202—C201—O205—C205	−62.5 (5)
O202—C202—C201—O205	−65.7 (6)
C203—C202—C201—O205	59.6 (5)
O203—C203—C202—C201	−176.8 (4)
C204—C203—C202—C201	−54.0 (5)
O204—C204—C203—C202	168.9 (3)
C205—C204—C203—C202	51.2 (5)
C206—C205—C204—C203	−170.6 (4)
O205—C205—C204—C203	−50.8 (5)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O102^{i}	0.98	2.12	2.973 (5)	145
O1—H1···O103^{i}	0.98	2.31	3.049 (7)	132
O1—H2···O206	1.05	1.73	2.750 (7)	163
O102—H1102···O203^{ii}	1.02	1.82	2.738 (6)	148
O103—H1103···O1	0.77	2.11	2.824 (7)	154
O104—H1104···O203^{iii}	0.97	2.07	2.925 (5)	146
O106—H1106···O204^{iv}	0.86	2.19	2.769 (5)	125
O202—H2202···O1	1.19	1.60	2.758 (5)	161
O203—H2203···O202^{v}	1.00	1.79	2.773 (7)	166
O204—H2204···O102^{vi}	1.08	1.93	2.894 (6)	146
O206—H2206···O106^{vi}	1.00	1.88	2.799 (6)	150
C206—H2061···O114^{vii}	0.97	2.66	3.372 (7)	130
C211—H211···O214^{viii}	0.96	2.50	3.403 (10)	157
C209—H209···C1001	0.99	2.87	3.441 (7)	118
C112—H112···C1002^{ix}	0.95	3.04	3.630 (6)	122

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, 2 - z$; (ii) $1 - x, \frac{1}{2} + y, 1 - z$; (iii) $1 - x, \frac{1}{2} + y, 2 - z$; (iv) $x, 1 + y, 1 + z$; (v) $1 - x, y - \frac{1}{2}, 1 - z$; (vi) $x, y - 1, z$; (vii) $-x, y - \frac{1}{2}, 1 - z$; (viii) $-x, y - \frac{1}{2}, -z$; (ix) $x, y, 1 + z$.

The structure was determined by direct methods. In the empirical weighting scheme, the coefficients of the quadratic functions $\chi(|F_o|)$ and $g(\sin\theta/\lambda)$ were chosen for groups of reflections in order to give no systematic trends in an analysis of variance.

Data collection: Philips PW1100 software. Cell refinement: *LSUCRE* (Appleman, 1995). Data reduction: *Xtal*3.2 *DIFDAT SORTRF ADDREF* (Hall, Flack & Stewart, 1994). Program(s) used to solve structure: *Xtal*3.2. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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