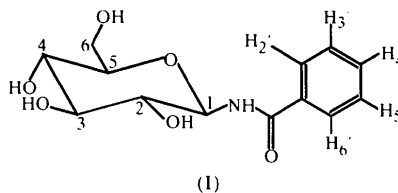


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## Comment

The vital roles played by glycoprotein glycans in many biological processes are well documented (Lis & Sharon, 1993). As part of our systematic study aimed at determining the three-dimensional structure of the linkage region in *N*-glycoproteins, we have previously described the crystal structure of the simplest model compound, *viz.*  $\beta$ -1-*N*-acetamido-D-glucopyranose (Sriram *et al.*, 1997). In continuation of this study, we report here on the crystal structure of the title compound, (I), chosen as an interesting hydrophobic analogue.



The *ORTEP*II (Johnson, 1976) plot of the benzamido derivative, giving the numbering scheme, is shown in Fig. 1. The pyranose ring adopts a <sup>4</sup>C<sub>1</sub>(*D*) chair conformation, with the values of the puckering parameters (Cremer & Pople, 1975) being  $Q = 0.566(4)$  Å,  $\theta = 173.4(4)^\circ$  and  $\varphi = 174(4)^\circ$ . The amide proton is *anti* with respect to its anomeric proton, with the H1—C1—N1—H1N torsion angle being  $-151^\circ$ . The benzamido group exists in the *Z-anti* conformation (H1N—N1—C1—O1' =  $171^\circ$ ). The above features, together with the pyranose ring bond lengths and angles and dihedral angles, are similar to those observed for the acetamido compound (Sriram *et al.*, 1997).

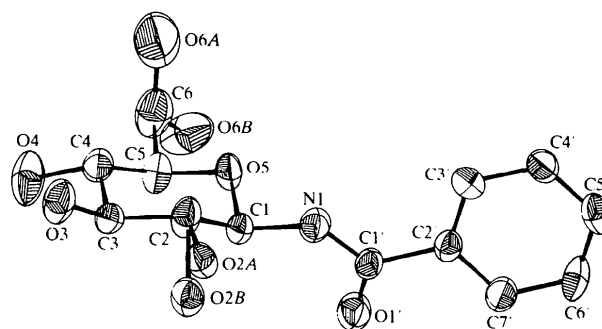


Fig. 1. *ORTEP*II (Johnson, 1976) plot, showing the molecular structure and atom-numbering scheme of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

*Acta Cryst.* (1998), **C54**, 1670–1672

 $\beta$ -1-*N*-Benzamido-D-glucopyranose

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(Received 5 January 1998; accepted 21 May 1998)

## Abstract

In the title compound, 1-benzamido- $\beta$ -D-glucopyranose, C<sub>13</sub>H<sub>17</sub>NO<sub>6</sub>, the pyranose ring adopts the <sup>4</sup>C<sub>1</sub>(*D*) conformation and the *N*-acetyl group exists in the *Z-anti* conformation. The primary alcohol group is disordered between the two permitted orientations, *gg* and *gt*.

The most interesting variation noticed in the crystal structure is the twofold disorder observed for the oxygen at C6. The partial occupancies for O6A and O6B are 0.71 (1) and 0.29 (1), respectively. The primary

alcohol group involving O6A adopts the *gg* conformation, whereas the one involving O6B takes up the *gt* conformation, as evident from the values of the torsion angles (O5/C4)—C5—C6—(O6A/O6B) (see Table 1). Such twofold disorder occurring between two permitted orientations has been observed previously in the crystal structures of  $\alpha$ -L-sorbopyranose and *meso*-erythritol (Jeffrey, 1990). The primary hydroxyl group takes up only the *gg* conformation in solution, as evident from the  $^1\text{H}$  NMR coupling constants,  $J_{6,5} = 2.0$  and  $J_{6',5} = 5.1$  Hz.

The O atom at C2 is also disordered, with O2A and O2B having occupancies of 0.62 (2) and 0.38 (2), respectively. The bond geometries involving both O6 and O2 show deviations from their ideal values, which are attributed to their large disorder and displacement parameters.

## Experimental

Perbenzoylation of  $\beta$ -D-glucopyranosylamine was performed following the literature procedure of Avalos *et al.* (1992). The product obtained was selectively de-O-benzoylated using sodium methoxide in dry methanol. Neutralization from IR-120 H<sup>+</sup> resin, followed by evaporation of the methanolic solution to dryness and crystallization from ethanol, afforded prismatic crystals of the title compound (m.p. 501 K).  $^1\text{H}$  NMR (400 MHz, D<sub>2</sub>O, p.p.m.):  $\delta$  7.85 (*d*, 2H,  $J = 7.3$  Hz, H3' and H7'), 7.66 (*t*, 1H,  $J = 7.6$  Hz, H5'), 7.56 (*t*, 2H,  $J = 7.6$  Hz, H4' and H6'), 5.23 (*d*, 1H,  $J = 8.8$  Hz, H1), 3.94 (*dd*, 1H,  $J_{6A,6B} = 12.2$ ,  $J_{6A,5} = 2.0$  Hz, H6A), 3.79 (*dd*, 1H,  $J_{6B,6A} = 12.2$ ,  $J_{6B,5} = 5.1$  Hz, H6B), 3.68–3.59 (*m*, 3H), 3.52 (*t*, 1H,  $J = 9.3$  Hz);  $^{13}\text{C}$  NMR (p.p.m.):  $\delta$  174.6 (–NHCO–), 135.5, 131.5, 130.3, 130.2, 82.7 (C1), 80.5, 79.4, 74.6, 72.1, 63.4 (C6).

### Crystal data

C<sub>13</sub>H<sub>17</sub>NO<sub>6</sub>  
 $M_r = 283.28$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 5.4367$  (7) Å  
 $b = 8.0061$  (8) Å  
 $c = 29.452$  (3) Å  
 $V = 1282.0$  (2) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.468$  Mg m<sup>−3</sup>  
 $D_m$  not measured

Cu K $\alpha$  radiation  
 $\lambda = 1.54180$  Å  
 Cell parameters from 25 reflections  
 $\theta = 8$ – $12^\circ$   
 $\mu = 0.991$  mm<sup>−1</sup>  
 $T = 293$  (2) K  
 Prismatic  
 $0.45 \times 0.42 \times 0.37$  mm  
 Colourless

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 1313 measured reflections  
 1313 independent reflections  
 1236 reflections with  $I > 2\sigma(I)$

$\theta_{\max} = 67.93^\circ$   
 $h = 0 \rightarrow 6$   
 $k = 0 \rightarrow 9$   
 $l = 0 \rightarrow 35$   
 2 standard reflections  
 frequency: 60 min  
 intensity decay: 3%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.055$   
 $wR(F^2) = 0.161$   
 $S = 1.085$   
 1313 reflections  
 198 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.1129P)^2 + 0.5341P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.737$  e Å<sup>−3</sup>  
 $\Delta\rho_{\min} = -0.198$  e Å<sup>−3</sup>  
 Extinction correction: SHELXL93  
 Extinction coefficient: 0.0158 (24)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.1 (6)

Table 1. Selected geometric parameters (Å, °)

C1—O5	1.420 (5)	C3—C4	1.512 (6)
C1—N1	1.435 (4)	C4—C5	1.524 (6)
C1—C2	1.518 (6)	C5—O5	1.427 (4)
C2—O2A	1.428 (6)	C6—O6B	1.356 (14)
C2—C3	1.509 (5)	C6—O6A	1.451 (11)
C2—O2B	1.539 (12)		
O2A—C2—C3	116.8 (4)	O6B—C6—O6A	128.5 (8)
O2A—C2—C1	115.6 (4)	O6B—C6—C5	111.2 (8)
C3—C2—O2B	98.1 (6)	O6A—C6—C5	109.1 (5)
C1—C2—O2B	99.5 (6)	C1—O5—C5	113.0 (3)
C1—N1—C1'—C2'	169.0 (3)	O5—C5—C6—O6B	80.3 (9)
N1—C1'—C2'—C7'	167.7 (3)	C4—C5—C6—O6B	−158.4 (8)
N1—C1'—C2'—C3'	−16.5 (5)	O5—C5—C6—O6A	−66.8 (5)
O5—C1—C2—C3	59.8 (4)	C4—C5—C6—O6A	54.4 (6)
C1—C2—C3—C4	−53.5 (4)	C2—C1—O5—C5	−64.9 (4)
C2—C3—C4—C5	50.2 (5)	C4—C5—O5—C1	59.6 (4)
C3—C4—C5—O5	−51.3 (4)		

H atoms were constrained. Those affected by disorder were not used in the refinement. The data faded rapidly at high angles.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: CAD-4 Software. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993).

The authors wish to thank the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, India, for data collection. Financial support from the Department of Science and Technology, New Delhi, India, is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1081). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). **C54**, 1672–1673

## 12,12-Ethylenedioxy-8 $\alpha$ ,9 $\alpha$ -epoxy-podocarpan-19-oic Acid†

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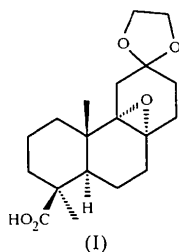
(Received 12 February 1998; accepted 11 June 1998)

### Abstract

The stereochemistry of the epoxide ring of the title compound, 12,12-ethylenedioxy-8 $\alpha$ ,9 $\alpha$ -epoxypodocarpan-19-oic acid, C<sub>19</sub>H<sub>28</sub>O<sub>5</sub>, prepared during studies aimed at converting podocarpic acid into precursors for the synthesis of biologically active quassinoids, has been confirmed by X-ray structure determination.

### Comment

During studies aimed at converting the natural product podocarpic acid into chiral precursors for the synthesis of biologically active quassinoids, we prepared an epoxide which was assigned the structure 12,12-ethylenedioxy-8 $\alpha$ ,9 $\alpha$ -podocarpan-19-oic acid, (I) (Cambie *et al.*, 1998). While products obtained from opening of the epoxide ring supported the assigned stereochemistry, a structural analysis was carried out on the epoxide in order to confirm the stereochemical assignment.



The structure confirms that the epoxide has 8 $\alpha$ ,9 $\alpha$  stereochemistry. The formation of the three-membered ring introduces some strain around C8 and C9, ev-

† Systematic name: 6,6-ethylenedioxy-1,4a-dimethyl-4b $\alpha$ ,8 $\alpha$ -epoxy-perhydropheanthrene-1-carboxylic acid.

idenced by the bond angles, which are up to 12.5° greater than the tetrahedral angle. The C8—C9 bond at 1.477(3) Å is long compared with the C—C bond in other epoxides, where the mean is 1.466 Å (Allen *et al.*, 1987). The increased distance is presumably due to the constraint imposed by the two fused six-membered rings where the epoxide lies across the ring junction. Other distances and angles are unexceptional. There is a hydrogen bond between the proton of the carboxylic acid group and an O atom of the dioxolane ring of an adjacent molecule [O4—O3' 2.720(2) Å; symmetry code: (i) 1 - x,  $\frac{1}{2}$  + y, 1 - z]. The absolute stereochemistry could not be determined and Fig. 1 shows the same stereochemistry as that of the parent podocarpic acid.

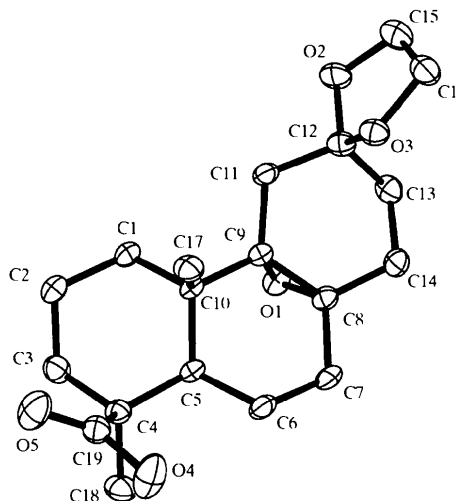


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

### Experimental

The title compound was obtained by epoxidation of 12,12-ethylenedioxy-podocarp-8-en-19-oic acid with *m*-chloroperbenzoic acid in a two-phase system of dichloromethane and 0.5 M aqueous sodium hydrogencarbonate. Chromatography on silica gel and elution with dichloromethane–ether (3:1) yielded the crystals of (I) (m.p. 455–458 K).

#### Crystal data

C<sub>19</sub>H<sub>28</sub>O<sub>5</sub>  
*M<sub>r</sub>* = 336.41  
 Monoclinic  
*P*2<sub>1</sub>  
*a* = 10.8912(6) Å  
*b* = 7.4907(4) Å  
*c* = 11.2879(6) Å  
 $\beta$  = 111.214(1)°  
*V* = 858.49(8) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.301 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 4922 reflections  
 $\theta$  = 2.0–27.5°  
 $\mu$  = 0.093 mm<sup>-1</sup>  
*T* = 203(2) K  
 Prism  
 0.60 × 0.45 × 0.40 mm  
 Colourless