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1-Amino-*N*,*N*-dibenzyl-1-deoxy-α-D-tagatopyranose methanol solvate

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Key indicators

Single-crystal X-ray study
T = 190 K
Mean σ(C–C) = 0.004 Å
R factor = 0.041
wR factor = 0.095
Data-to-parameter ratio = 10.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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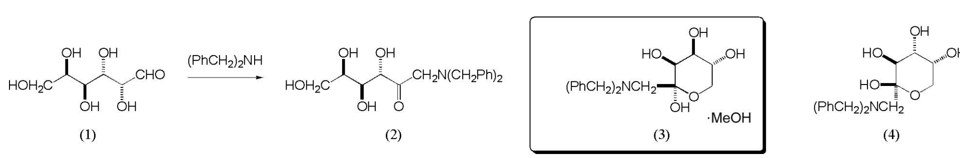
The title tagatosamine, $C_{20}H_{25}NO_5.CH_4O$, formed in the Amadori rearrangement of D-galactose with dibenzylamine, is shown to crystallize as the α-anomer, in contrast to the β-anomer formed in the Amadori reaction of D-glucose with dibenzylamine.

Comment

The Amadori rearrangement, an old and well known reaction (Amadori, 1925; Hodge, 1955), constitutes the first step in the Maillard reaction (Maillard, 1912), the classic browning reaction of food chemistry and one of the most complex reactions known (Martins & Van Boekel, 2005; Kwak & Lim, 2004). Products of the Maillard reaction are responsible for much of the flavour and colour generated during baking and roasting (Mottram *et al.*, 2002). Despite its long standing, however, both the full synthetic potential of the Amadori rearrangement and its role in pathology have yet to be fully understood. The rearrangement is the initial step in the non-enzymatic conjugation of free amines in peptides with reducing carbohydrates to form glycation products *in vivo*; such advanced glycation end-products (AGE) constitute a complex and heterogeneous group of compounds which accumulate in plasma and tissues in diabetes and renal failure (Lapolla *et al.*, 2005; Smit & Lutgers, 2004). Non-enzymatic glycation has also been implicated in processes of ageing, atherosclerosis and in neurodegenerative amyloid pathologies, including Alzheimer's disease (Horvat & Jakas, 2004; Kikuchi *et al.*, 2003).



D-Galactose (1) on treatment with dibenzylamine in acetic acid, underwent the Amadori rearrangement to give tagatosamine (2) (Grünnagel & Haas, 1969); although the solution NMR of (2) was complex, the formation of crystals allowed the secure identification of the α-anomer (3). Crystallization of the α-anomer of tagatosamine is in direct contrast to the crystallization of the β-anomer of fructosamine (4), the Amadori product formed from D-glucose and dibenzylamine (Hou *et al.*, 2001).

The molecules form independent hydrogen-bonded chains parallel to the b axis, incorporating the solvent in the extensive hydrogen-bonding network (Fig. 2).

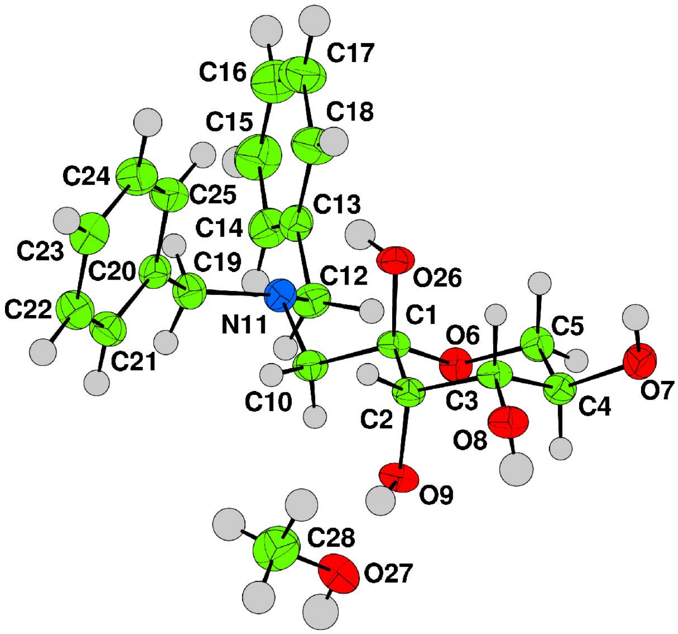


Figure 1
The title compound, with displacement ellipsoids drawn at the 50% probability level.

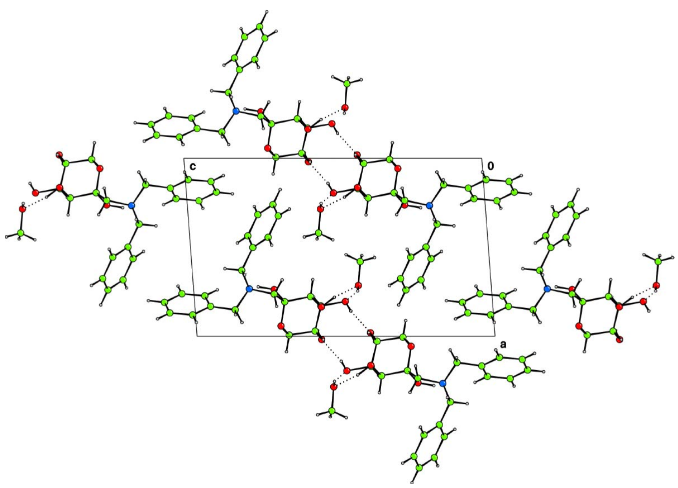


Figure 2
The crystal packing, viewed down the *b* axis.

Experimental

Crystals of the title compound were first obtained by evaporation of a solution in a methanol–water mixture. They were then recrystallized from hot methanol to afford colourless crystals. The full synthetic procedure will be published separately (Hotchkiss *et al.*, 2005).

Crystal data

$C_{20}H_{25}NO_5 \cdot CH_4O$	D_x = 1.239 Mg m^{-3}
M_r = 391.46	Mo Kα radiation
Monoclinic, $P2_1$	Cell parameters from 2207 reflections
a = 10.3116 (3) Å	θ = 1–27°
b = 5.9084 (2) Å	μ = 0.09 mm^{-1}
c = 17.2641 (6) Å	T = 190 K
β = 94.2891 (13)°	Block, colourless
V = 1048.87 (6) Å^3	0.18 × 0.18 × 0.10 mm
Z = 2	

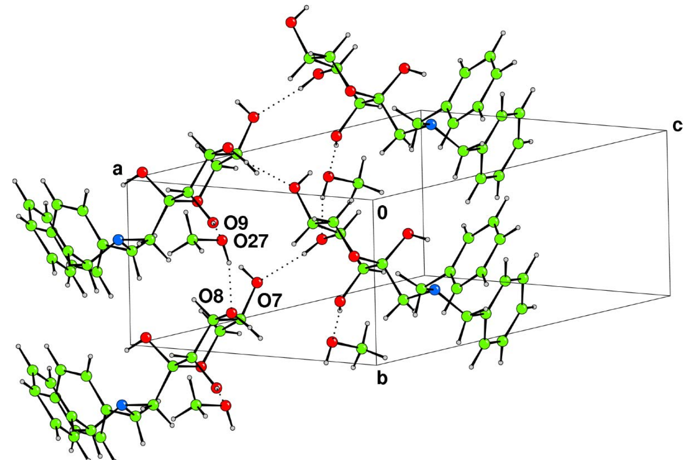


Figure 3
View of a section of one hydrogen-bonded (dashed lines) chain, showing how the solvent and main molecule interact to form the chain.

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.019
ω scans	θ_{max} = 27.5°
Absorption correction: none	$h = -13 \rightarrow 13$
4394 measured reflections	$k = -7 \rightarrow 7$
2601 independent reflections	$l = -22 \rightarrow 22$
2044 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.24P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.041	where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$wR(F^2)$ = 0.095	$(\Delta/\sigma)_{max} < 0.001$
S = 0.90	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
2588 reflections	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
253 parameters	
H-atom parameters constrained	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O27—H1···O8^{i}	0.84	1.89	2.700 (3)	161
O7—H4···O9^{ii}	0.78	2.00	2.740 (2)	157
O8—H12···O7^{iii}	0.82	1.95	2.756 (2)	167
O9—H253···O27	0.96	1.77	2.692 (2)	159

Symmetry codes: (i) $x, 1+y, z$; (ii) $x, y-1, z$; (iii) $-x, \frac{1}{2}+y, 1-z$.

All of the H atoms were observed in a difference electron-density map. The hydroxyl H atoms were placed as found and the others were positioned geometrically (C—H = 1.0 Å). All were refined with slack restraints and with U_{iso}(H) = 1.2U_{eq}(parent atom), and then refined as riding atoms. In the absence of significant scattering effects, Friedel pairs were merged. The final structure shows voids of 50 Å^3 to be present. These regions were investigated with difference electron-density maps, but no electron density was found within them. Four reflections were removed manually as outliers, whilst some low-angle reflections were omitted from the refinement because they appeared to be obscured by the beam-stop.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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