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1-Amino-*N*,*N*-dibenzyl-1,6-dideoxy-β-L-fructofuranose

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Key indicators

Single-crystal X-ray study
T = 190 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.078
Data-to-parameter ratio = 9.9

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

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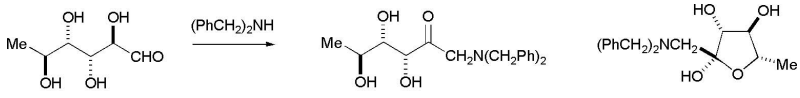
The title compound, $C_{20}H_{25}NO_4$, the product formed in the Amadori rearrangement of L-rhamnose with dibenzylamine, is shown by X-ray crystallographic analysis to be a rare example of an Amadori product crystallizing in a furanose form.

Comment

The Amadori rearrangement, an old and complex reaction (Amadori, 1925; Hodge, 1955), is the initial step in the non-enzymatic conjugation of free amines in peptides with reducing carbohydrates to form glycation products; such materials 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 and in neurodegenerative amyloid pathologies, including Alzheimer's disease (Horvat & Jakas, 2004). Amadori ketoses are also the starting materials for the Maillard reaction (O'Brien *et al.*, 1998), the classic browning reaction of food chemistry (Martins & Van Boekel, 2005; Kwak & Lim, 2004).



(1) (2) (3)

L-Rhamnose, (1), on treatment with dibenzylamine in acetic acid, undergoes the Amadori rearrangement to give the

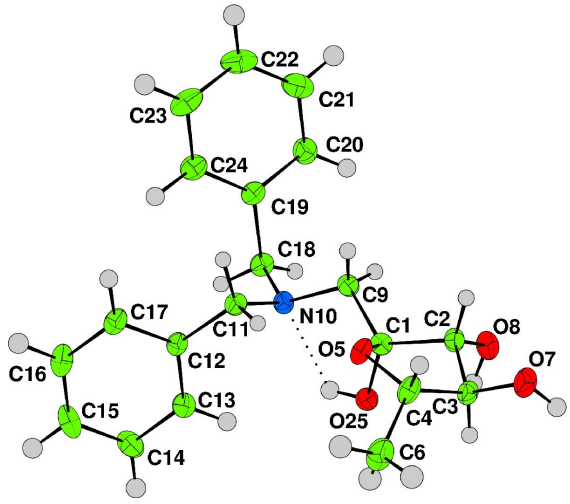


Figure 1
The molecular structure of (3), with displacement ellipsoids drawn at the 50% probability level. Also shown is an intramolecular hydrogen bond (dotted line), forming a five-membered ring with atom C9 displaced from its mean plane.

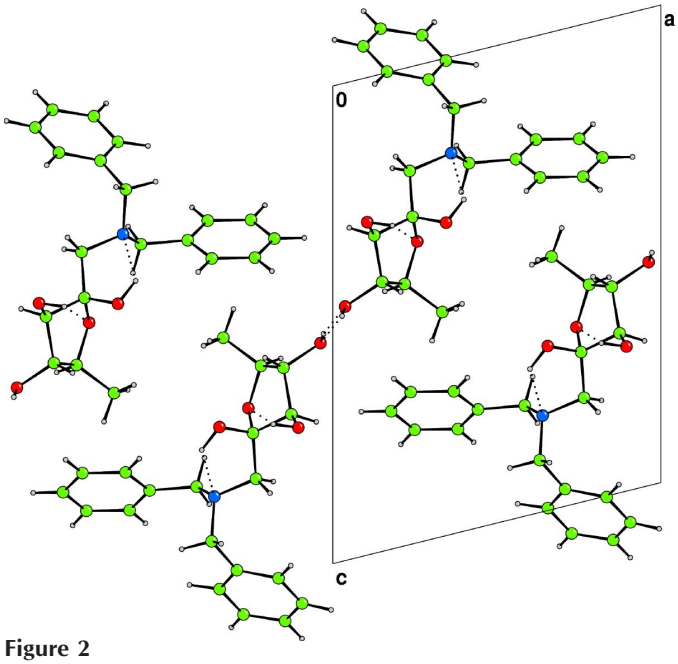


Figure 2
Packing diagram for the title compound, viewed down the *b* axis. The crystal structure is made up of columns of strongly hydrogen-bonded (dotted lines) molecules which run along the *b* axis.

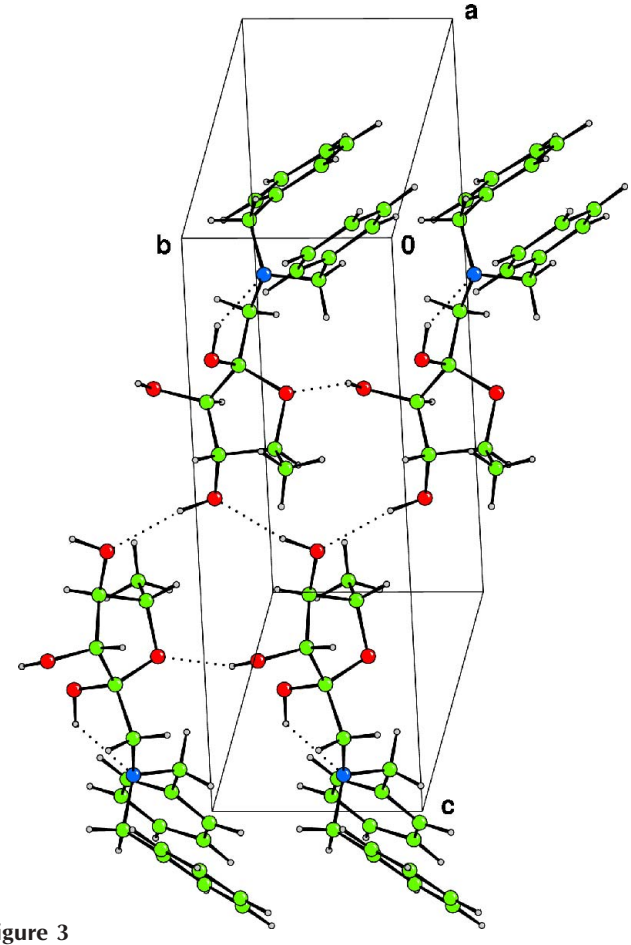


Figure 3
A view of the hydrogen-bonding (dotted lines) network in each column. Hydrogen bonds involving atom O7 form a central chain up the column, with hydrogen bonds to the furanose ring O atom from hydroxyl groups on different molecules adding support to the structure.

ketoseamine (2) (Funcke, 1978); although the solution NMR of (2) is complex and indicates a mixture of forms, the formation of crystals allowed the secure identification of the β-anomer (3). There is one other example of a crystal structure of a furanose Amadori product (Fernández-Bolaños *et al.*, 2003).

Experimental

Crystals of the title compound were first obtained using evaporation techniques from a methanol–water mixture. They were then recrystallized from a diethyl ether/petrol solvent mixture. This yielded thin needle-like colourless crystals.

Crystal data

$C_{20}H_{25}NO_4$
M_r = 343.42
Monoclinic, $P2_1$
a = 10.8823 (2) Å
b = 5.4690 (1) Å
c = 15.3816 (2) Å
β = 103.8824 (11)°
V = 888.70 (3) Å^3
Z = 2
D_x = 1.283 Mg m^{-3}
Mo Kα radiation
Cell parameters from 2070 reflections
θ = 1–27°
μ = 0.09 mm^{-1}
T = 190 K
Block cut from needle, colourless
0.20 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.98, T_{max} = 0.99
3627 measured reflections
2237 independent reflections
1942 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 27.5°
$h = -13 \rightarrow 14$
$k = -7 \rightarrow 6$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.078
S = 0.99
2229 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.09P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O25—H5···N10	0.94	2.06	2.6725 (19)	121
O7—H17···O7^{i}	0.95	2.15	3.080 (2)	166
O8—H24···O5^{ii}	0.98	2.02	2.883 (2)	147

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

All H atoms were observed in a difference electron-density map. The hydroxyl H atoms were refined freely, whilst the others were refined with slack restraints to optimize the geometry (C—H = 1.0 Å). All were then made to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(parent). In the absence of significant anomalous scattering effects, Friedel pairs were merged; the absolute configuration is known from the synthesis. Several low-angle reflections were omitted from the refinement because they appeared to be obscured by the beam stop.

Data collection: *COLLECT* (Nonius, 2001); 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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supporting information

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Cell parameters from 2070 reflections
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$\mu = 0.09$ mm^{-1}
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Data collection

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$h = -13 \rightarrow 14$
$k = -7 \rightarrow 6$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.078$
$S = 0.99$
2229 reflections
226 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.09P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.000163$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.24341 (16)	0.8449 (4)	0.31483 (11)	0.0213
C2	0.12615 (16)	0.9649 (4)	0.33411 (11)	0.0236

C3	0.15036 (16)	0.9307 (4)	0.43567 (11)	0.0242
C4	0.21898 (18)	0.6849 (4)	0.45156 (11)	0.0281
O5	0.25760 (12)	0.6297 (3)	0.36919 (7)	0.0248
C6	0.3337 (2)	0.6780 (6)	0.52978 (12)	0.0466
O7	0.03752 (11)	0.9209 (3)	0.46816 (8)	0.0346
O8	0.10507 (12)	1.2076 (3)	0.30281 (9)	0.0303
C9	0.23408 (15)	0.7756 (4)	0.21732 (10)	0.0237
N10	0.36084 (13)	0.7409 (3)	0.20179 (9)	0.0216
C11	0.41506 (16)	0.5005 (4)	0.23173 (11)	0.0225
C12	0.55810 (16)	0.4956 (4)	0.24789 (10)	0.0217
C13	0.63127 (17)	0.6773 (4)	0.29832 (12)	0.0303
C14	0.76282 (18)	0.6647 (5)	0.31904 (13)	0.0350
C15	0.82190 (18)	0.4696 (5)	0.28901 (13)	0.0348
C16	0.75082 (19)	0.2890 (5)	0.23788 (13)	0.0351
C17	0.61897 (18)	0.3026 (4)	0.21695 (12)	0.0287
C18	0.36926 (16)	0.8006 (4)	0.10956 (10)	0.0237
C19	0.29227 (16)	0.6416 (4)	0.03600 (10)	0.0228
C20	0.16543 (17)	0.6949 (5)	−0.00240 (11)	0.0305
C21	0.09348 (19)	0.5435 (5)	−0.06740 (12)	0.0380
C22	0.1456 (2)	0.3377 (5)	−0.09546 (13)	0.0405
C23	0.2722 (2)	0.2853 (5)	−0.06025 (12)	0.0382
C24	0.34477 (19)	0.4358 (4)	0.00519 (12)	0.0299
O25	0.34520 (11)	1.0063 (3)	0.34463 (7)	0.0254
H21	0.0504	0.8672	0.3054	0.0288*
H31	0.2068	1.0624	0.4661	0.0296*
H41	0.1588	0.5572	0.4566	0.0364*
H61	0.3751	0.5183	0.5300	0.0556*
H62	0.3026	0.6978	0.5844	0.0566*
H63	0.3937	0.8124	0.5229	0.0561*
H91	0.1915	0.9117	0.1800	0.0282*
H92	0.1816	0.6317	0.2028	0.0294*
H111	0.3763	0.3712	0.1885	0.0267*
H112	0.3912	0.4659	0.2882	0.0267*
H131	0.5898	0.8162	0.3198	0.0376*
H141	0.8142	0.7941	0.3558	0.0424*
H151	0.9131	0.4603	0.3033	0.0431*
H161	0.7926	0.1520	0.2146	0.0455*
H171	0.5711	0.1722	0.1815	0.0353*
H181	0.3400	0.9716	0.0994	0.0278*
H182	0.4603	0.7958	0.1085	0.0274*
H201	0.1281	0.8398	0.0176	0.0366*
H211	0.0053	0.5826	−0.0959	0.0449*
H221	0.0939	0.2280	−0.1409	0.0483*
H231	0.3093	0.1398	−0.0810	0.0465*
H241	0.4367	0.3980	0.0297	0.0368*
H5	0.3992	0.9894	0.3057	0.0365*
H17	0.0279	1.0853	0.4862	0.0386*
H24	0.1815	1.3054	0.3228	0.0377*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0219 (8)	0.0200 (10)	0.0225 (8)	−0.0015 (8)	0.0060 (6)	0.0017 (8)
C2	0.0215 (8)	0.0222 (11)	0.0277 (9)	0.0022 (8)	0.0073 (7)	−0.0009 (8)
C3	0.0231 (8)	0.0249 (11)	0.0272 (9)	−0.0015 (9)	0.0115 (7)	−0.0040 (9)
C4	0.0382 (10)	0.0255 (11)	0.0262 (9)	0.0022 (10)	0.0186 (8)	0.0017 (9)
O5	0.0348 (7)	0.0195 (8)	0.0234 (6)	0.0046 (6)	0.0134 (5)	0.0005 (6)
C6	0.0588 (13)	0.0569 (17)	0.0237 (9)	0.0256 (15)	0.0090 (9)	0.0037 (11)
O7	0.0309 (7)	0.0400 (10)	0.0398 (7)	−0.0031 (7)	0.0219 (6)	−0.0066 (7)
O8	0.0276 (7)	0.0260 (8)	0.0378 (7)	0.0059 (7)	0.0089 (5)	0.0043 (7)
C9	0.0204 (8)	0.0289 (11)	0.0217 (8)	0.0012 (9)	0.0045 (6)	−0.0011 (9)
N10	0.0210 (7)	0.0270 (10)	0.0181 (6)	0.0027 (7)	0.0070 (5)	0.0017 (7)
C11	0.0240 (9)	0.0212 (11)	0.0229 (8)	−0.0007 (8)	0.0072 (6)	−0.0004 (8)
C12	0.0252 (9)	0.0215 (10)	0.0193 (8)	0.0033 (9)	0.0070 (6)	0.0019 (8)
C13	0.0276 (9)	0.0281 (12)	0.0336 (9)	0.0041 (10)	0.0042 (7)	−0.0045 (10)
C14	0.0250 (9)	0.0351 (13)	0.0417 (11)	0.0008 (10)	0.0015 (8)	0.0018 (11)
C15	0.0236 (9)	0.0386 (14)	0.0443 (11)	0.0089 (10)	0.0119 (8)	0.0143 (11)
C16	0.0375 (11)	0.0339 (13)	0.0386 (10)	0.0103 (11)	0.0186 (9)	0.0039 (11)
C17	0.0355 (10)	0.0242 (11)	0.0278 (9)	0.0055 (9)	0.0101 (7)	−0.0014 (9)
C18	0.0266 (9)	0.0249 (11)	0.0213 (8)	−0.0022 (9)	0.0088 (7)	0.0011 (8)
C19	0.0283 (9)	0.0232 (11)	0.0186 (8)	−0.0009 (9)	0.0089 (7)	0.0024 (8)
C20	0.0285 (9)	0.0390 (13)	0.0258 (8)	0.0022 (10)	0.0099 (7)	0.0009 (10)
C21	0.0312 (10)	0.0544 (17)	0.0275 (10)	−0.0103 (11)	0.0054 (8)	0.0000 (11)
C22	0.0497 (13)	0.0462 (16)	0.0245 (9)	−0.0176 (13)	0.0065 (8)	−0.0026 (10)
C23	0.0595 (13)	0.0305 (13)	0.0267 (9)	−0.0037 (12)	0.0149 (9)	−0.0036 (10)
C24	0.0360 (10)	0.0308 (12)	0.0239 (9)	−0.0003 (10)	0.0088 (7)	0.0006 (9)
O25	0.0211 (6)	0.0288 (8)	0.0274 (6)	−0.0033 (6)	0.0080 (5)	−0.0040 (6)

Geometric parameters (Å, º)

C1—C2	1.526 (3)	C12—C13	1.388 (3)
C1—O5	1.430 (2)	C12—C17	1.389 (3)
C1—C9	1.527 (2)	C13—C14	1.392 (3)
C1—O25	1.405 (2)	C13—H131	0.980
C2—C3	1.532 (2)	C14—C15	1.382 (3)
C2—O8	1.412 (3)	C14—H141	0.990
C2—H21	0.993	C15—C16	1.379 (3)
C3—C4	1.529 (3)	C15—H151	0.965
C3—O7	1.433 (2)	C16—C17	1.395 (3)
C3—H31	0.989	C16—H161	0.987
C4—O5	1.4589 (19)	C17—H171	0.970
C4—C6	1.512 (3)	C18—C19	1.511 (3)
C4—H41	0.973	C18—H181	0.988
C6—H61	0.982	C18—H182	0.995
C6—H62	0.984	C19—C20	1.396 (2)
C6—H63	1.005	C19—C24	1.395 (3)
O7—H17	0.954	C20—C21	1.387 (3)

O8—H24	0.975	C20—H201	0.974
C9—N10	1.468 (2)	C21—C22	1.375 (4)
C9—H91	0.985	C21—H211	0.978
C9—H92	0.966	C22—C23	1.384 (3)
N10—C11	1.469 (3)	C22—H221	0.988
N10—C18	1.480 (2)	C23—C24	1.391 (3)
C11—C12	1.516 (2)	C23—H231	0.980
C11—H111	0.993	C24—H241	1.003
C11—H112	0.983	O25—H5	0.939

C2—C1—O5	102.6 (1)	C12—C11—H112	109.3
C2—C1—C9	115.9 (1)	H111—C11—H112	107.2
O5—C1—C9	110.0 (2)	C11—C12—C13	120.5 (2)
C2—C1—O25	107.3 (2)	C11—C12—C17	120.8 (2)
O5—C1—O25	111.1 (1)	C13—C12—C17	118.6 (2)
C9—C1—O25	109.8 (1)	C12—C13—C14	120.9 (2)
C1—C2—C3	101.5 (1)	C12—C13—H131	119.6
C1—C2—O8	114.4 (2)	C14—C13—H131	119.5
C3—C2—O8	115.9 (2)	C13—C14—C15	119.8 (2)
C1—C2—H21	109.0	C13—C14—H141	120.3
C3—C2—H21	108.1	C15—C14—H141	119.9
O8—C2—H21	107.7	C14—C15—C16	120.1 (2)
C2—C3—C4	103.2 (2)	C14—C15—H151	120.0
C2—C3—O7	114.1 (1)	C16—C15—H151	119.8
C4—C3—O7	109.8 (2)	C15—C16—C17	119.9 (2)
C2—C3—H31	109.3	C15—C16—H161	120.5
C4—C3—H31	109.9	C17—C16—H161	119.6
O7—C3—H31	110.4	C16—C17—C12	120.7 (2)
C3—C4—O5	105.9 (2)	C16—C17—H171	118.3
C3—C4—C6	115.3 (2)	C12—C17—H171	121.0
O5—C4—C6	109.3 (2)	N10—C18—C19	116.1 (2)
C3—C4—H41	109.4	N10—C18—H181	105.6
O5—C4—H41	105.1	C19—C18—H181	109.0
C6—C4—H41	111.2	N10—C18—H182	107.5
C4—O5—C1	108.9 (1)	C19—C18—H182	110.4
C4—C6—H61	108.3	H181—C18—H182	107.9
C4—C6—H62	106.8	C18—C19—C20	120.7 (2)
H61—C6—H62	110.2	C18—C19—C24	121.3 (2)
C4—C6—H63	109.4	C20—C19—C24	118.0 (2)
H61—C6—H63	110.0	C19—C20—C21	120.7 (2)
H62—C6—H63	112.0	C19—C20—H201	118.8
C3—O7—H17	103.2	C21—C20—H201	120.5
C2—O8—H24	110.6	C20—C21—C22	120.7 (2)
C1—C9—N10	110.4 (1)	C20—C21—H211	121.1
C1—C9—H91	107.2	C22—C21—H211	118.2
N10—C9—H91	109.3	C21—C22—C23	119.6 (2)
C1—C9—H92	109.0	C21—C22—H221	120.7
N10—C9—H92	112.6	C23—C22—H221	119.7

H91—C9—H92	108.2	C22—C23—C24	120.0 (2)
C9—N10—C11	112.8 (2)	C22—C23—H231	119.3
C9—N10—C18	113.9 (1)	C24—C23—H231	120.6
C11—N10—C18	112.7 (2)	C19—C24—C23	121.0 (2)
N10—C11—C12	112.7 (2)	C19—C24—H241	119.5
N10—C11—H111	110.7	C23—C24—H241	119.5
C12—C11—H111	110.6	C1—O25—H5	107.2
N10—C11—H112	106.1		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O25—H5···N10	0.94	2.06	2.6725 (19)	121
O7—H17···O7^{i}	0.95	2.15	3.080 (2)	166
O8—H24···O5^{ii}	0.98	2.02	2.883 (2)	147

Symmetry codes: (i) −*x*, *y*+1/2, −*z*+1; (ii) *x*, *y*+1, *z*.