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 α -D-TagatopyranoseFrancesco Punzo,^{a,*} David J. Watkin^b and George W. J. Fleet^c

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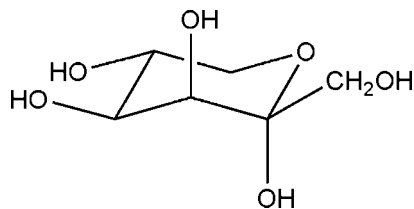
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Key indicators: single-crystal X-ray study; $T = 190$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.025; wR factor = 0.065; data-to-parameter ratio = 12.5.

The title compound, $\text{C}_6\text{H}_{12}\text{O}_6$, also known as D-Tagatose, occurs in its furanose and pyranose forms in solution, but only the α -pyranose form crystallizes out. In the crystal, the molecules form hydrogen bonded chains propagating in [100] linked by $\text{O}-\text{H}\cdots\text{O}$ interactions. Further $\text{O}-\text{H}\cdots\text{O}$ bonds cross-link the chains.

Related literature

For the D-tagatose market price, syntheses and applications, see: Angyal (1991); Beadle *et al.* (1992); Granstrom *et al.* (2004); Izumori (2002); Skytte (2002); Porwell (2007). For the potential of the title compound as a chiral building block, see: Soengas *et al.* (2005); Jones *et al.* (2007, 2008); Yoshihara *et al.* (2008). For related crystallographic literature, see: Takagi *et al.* (1969); Görbitz (1999); Watkin *et al.* (2005); Kwiecien *et al.* (2008); Larson (1970).



Experimental

Crystal data

$\text{C}_6\text{H}_{12}\text{O}_6$ $b = 6.5022$ (1) Å
 $M_r = 180.16$ $c = 17.6629$ (4) Å
 Orthorhombic, $P2_12_12_1$ $V = 714.36$ (2) Å³
 $a = 6.2201$ (1) Å $Z = 4$

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Mo $K\alpha$ radiation
 $\mu = 0.15$ mm⁻¹

$T = 190$ K
 $0.50 \times 0.30 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer 2343 measured reflections
 Absorption correction: multi-scan 1378 independent reflections
 (DENZO/SCALEPACK; 1351 reflections with $I > 2.0\sigma(I)$)
 Otwinowski & Minor, 1997) $R_{\text{int}} = 0.010$
 $T_{\text{min}} = 0.96$, $T_{\text{max}} = 0.97$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$ 110 parameters
 $wR(F^2) = 0.065$ H-atom parameters constrained
 $S = 0.96$ $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 1378 reflections $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O4—H41...O1 ⁱ	0.81	2.02	2.8236 (14)	171
O9—H91...O1 ⁱⁱ	0.83	1.90	2.7203 (14)	173
O12—H121...O4 ⁱⁱⁱ	0.83	2.09	2.7875 (14)	142
O10—H101...O4 ^{iv}	0.81	2.10	2.8518 (14)	155
O1—H11...O6 ^v	0.81	1.96	2.7661 (14)	175

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

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.

Arla Foods generously provided a sample of D-tagatose, obtained as described (Beadle *et al.*, 1992) from D-galactose, for crystallization.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2248).

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supplementary materials

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α -D-Tagatopyranose

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Comment

Until recently *D*-tagatose was a rare and expensive hexose; the price in the 2007–2008 Aldrich catalogue was 331.00 pounds sterling for 5 g (Porwell, 2007). It is now available cheaply in large quantities [around 5 pounds sterling per kg] prepared by either chemical (Beadle *et al.*, 1992) or biotechnological (Granstrom *et al.*, 2004; Izumori, 2002) techniques, and it is widely investigated as a low calorie sweetener (Skytte, 2002); the potential of *D*-tagatose as a chiral building block is also beginning to be recognized (Soengas *et al.*, 2005; Watkin *et al.*, 2005; Jones *et al.*, 2007; Jones *et al.*, 2008; Yoshihara *et al.*, 2008). The crystal structure of another hitherto rare diastereoisomeric ketohexose, *D*-psicose, has recently been published (Kwiecien *et al.*, 2008). A previous α -*D*-tagatose structure solution (Takagi *et al.*, 1969), did not report either three-dimensional coordinates or bond lengths and angles. Although in aqueous solution both furanose and pyranose forms are present, only the α -pyranose crystallizes out. The crystal structure of the title compound (Fig. 1) consists of a network of hydrogen-bonded chains running parallel to the *a* axis (Fig.2). Referring to Table 1, O4—H41 \cdots O10 is the only intramolecular hydrogen bond detected in the structure. O12—H121 \cdots O4 and O1—H11 \cdots O6 link the molecules into chains, and O9—H91 \cdots O1 and O10—H101 \cdots O4 stabilize the structure with inter-chain hydrogen bonds. O4 is involved as an acceptor in two hydrogen bonds and as a donor in an almost linear hydrogen bond - the latter by means of H41. The crystal structure shows three equatorial groups and two axial groups, one of which is an axial anomeric hydroxyl group; this would be expected to be the most thermodynamically stable pyranose anomer. The fairly high value of the anisotropic displacement of O12 - compared to the other C and O atoms - is probably due to thermal motion. It results also in a higher - compared to the other H atoms - isotropic displacement for H121 *i.e.* the hydrogen atom connected to the last atom of the flexible C7—C11—O12 chain.




Experimental

In aqueous solution the major form present is α -*D*-tagatopyranose (71%) (Fig.1) with 18% of the β -pyranose and small amount of the furanoses (Angyal, 1991). The title compound was recrystallized from a 1:10 mixture of water and acetone allowing the slow competitive evaporation of the solvents, after which, transparent prismatic crystals appeared.

Refinement

The data were collected with molybdenum radiation and since there were no atoms heavier than Si present, there were no measurable anomalous differences and it was admissible to merge Friedel pairs of reflections. Changes in illuminated volume were kept to a minimum, and were taken into account (Görbitz, 1999) by the multi-scan inter-frame scaling (*DENZO/SCALEPACK*, Otwinowski & Minor, 1997). The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 O—H = 0.82 Å) and $U_{\text{iso}}(\text{H})$ (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Figures

-  Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.
-  Fig. 2. Packing diagram of title compound viewed down the *a* axis. Hydrogen bonds are shown as dotted lines.
-  Fig. 3. D-Tagatose and α -D-tagatopyranose.

α -D-Tagatopyranose

Crystal data

$C_6H_{12}O_6$	$F_{000} = 384$
$M_r = 180.16$	$D_x = 1.675 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
Hall symbol: P 2ac 2ab	$\lambda = 0.71073 \text{ \AA}$
$a = 6.2201 (1) \text{ \AA}$	Cell parameters from 1344 reflections
$b = 6.5022 (1) \text{ \AA}$	$\theta = 5\text{--}32^\circ$
$c = 17.6629 (4) \text{ \AA}$	$\mu = 0.15 \text{ mm}^{-1}$
$V = 714.36 (2) \text{ \AA}^3$	$T = 190 \text{ K}$
$Z = 4$	Prism, colourless
	$0.50 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer	1351 reflections with $I > 2.0\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.010$
$T = 190 \text{ K}$	$\theta_{\text{max}} = 31.5^\circ$
ω scans	$\theta_{\text{min}} = 5.6^\circ$
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.96, T_{\text{max}} = 0.97$	$k = -9 \rightarrow 9$
2343 measured reflections	$l = -25 \rightarrow 25$
1378 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.025$	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.18P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$
$wR(F^2) = 0.065$	$(\Delta/\sigma)_{\text{max}} = 0.0001$
$S = 0.97$	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$

1378 reflections

$$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$$

110 parameters

Extinction correction: Larson (1970), Equation 22

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 260 (40)

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	-0.20580 (13)	0.34108 (12)	0.17994 (4)	0.0157
C2	-0.02883 (15)	0.29006 (15)	0.13171 (5)	0.0113
C3	0.10689 (16)	0.47890 (15)	0.11569 (5)	0.0118
O4	-0.02429 (12)	0.62640 (12)	0.07662 (4)	0.0150
C5	0.29501 (17)	0.41697 (16)	0.06531 (6)	0.0143
O6	0.42202 (12)	0.25811 (12)	0.09985 (4)	0.0139
C7	0.30499 (16)	0.07510 (15)	0.11774 (5)	0.0118
C8	0.11083 (16)	0.12491 (15)	0.16890 (5)	0.0118
O9	0.18387 (14)	0.19838 (12)	0.24031 (4)	0.0171
O10	0.22054 (13)	-0.01458 (12)	0.05105 (4)	0.0142
C11	0.46654 (17)	-0.06848 (16)	0.15537 (6)	0.0155
O12	0.61351 (15)	-0.12797 (16)	0.09805 (5)	0.0271
H21	-0.0851	0.2365	0.0849	0.0134*
H31	0.1585	0.5338	0.1629	0.0151*
H51	0.3943	0.5322	0.0579	0.0174*
H52	0.2364	0.3698	0.0173	0.0181*
H81	0.0263	0.0023	0.1724	0.0147*
H112	0.5375	-0.0021	0.1979	0.0193*
H111	0.3929	-0.1876	0.1738	0.0194*
H41	0.0463	0.7255	0.0642	0.0240*
H91	0.1860	0.0956	0.2678	0.0275*
H121	0.7044	-0.2120	0.1130	0.0413*
H101	0.3225	-0.0416	0.0248	0.0252*
H11	-0.3163	0.3242	0.1565	0.0238*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0103 (3)	0.0192 (4)	0.0177 (3)	-0.0009 (3)	0.0026 (3)	-0.0047 (3)
C2	0.0102 (4)	0.0120 (4)	0.0118 (4)	-0.0005 (4)	0.0005 (3)	-0.0019 (3)
C3	0.0107 (4)	0.0107 (4)	0.0141 (4)	0.0001 (3)	-0.0003 (3)	0.0004 (3)
O4	0.0131 (3)	0.0119 (3)	0.0201 (3)	0.0026 (3)	-0.0007 (3)	0.0027 (3)
C5	0.0125 (4)	0.0121 (4)	0.0183 (4)	0.0022 (4)	0.0034 (4)	0.0041 (3)
O6	0.0097 (3)	0.0111 (3)	0.0209 (3)	-0.0001 (3)	-0.0007 (3)	0.0036 (3)
C7	0.0112 (4)	0.0100 (4)	0.0143 (4)	-0.0003 (4)	-0.0007 (3)	0.0007 (3)
C8	0.0124 (4)	0.0107 (4)	0.0122 (4)	-0.0020 (4)	-0.0001 (3)	-0.0004 (3)
O9	0.0243 (4)	0.0154 (3)	0.0115 (3)	-0.0007 (3)	-0.0033 (3)	0.0001 (3)
O10	0.0138 (3)	0.0151 (3)	0.0137 (3)	0.0009 (3)	0.0005 (3)	-0.0030 (3)
C11	0.0136 (4)	0.0139 (4)	0.0191 (4)	0.0026 (4)	-0.0015 (4)	0.0033 (4)
O12	0.0213 (4)	0.0322 (5)	0.0280 (4)	0.0161 (4)	0.0044 (4)	0.0078 (4)

supplementary materials

Geometric parameters (Å, °)

O1—C2	1.4309 (12)	O6—C7	1.4303 (12)
O1—H11	0.810	C7—C8	1.5426 (14)
C2—C3	1.5167 (14)	C7—O10	1.4155 (12)
C2—C8	1.5294 (14)	C7—C11	1.5241 (14)
C2—H21	0.963	C8—O9	1.4232 (11)
C3—O4	1.4359 (12)	C8—H81	0.957
C3—C5	1.5241 (14)	O9—H91	0.826
C3—H31	0.963	O10—H101	0.805
O4—H41	0.810	C11—O12	1.4178 (14)
C5—O6	1.4364 (12)	C11—H112	0.973
C5—H51	0.980	C11—H111	0.957
C5—H52	0.972	O12—H121	0.829
C2—O1—H11	108.5	O6—C7—C8	110.68 (8)
O1—C2—C3	110.58 (8)	O6—C7—O10	110.35 (8)
O1—C2—C8	110.13 (8)	C8—C7—O10	106.46 (8)
C3—C2—C8	109.41 (8)	O6—C7—C11	105.69 (8)
O1—C2—H21	108.4	C8—C7—C11	112.92 (8)
C3—C2—H21	109.6	O10—C7—C11	110.81 (8)
C8—C2—H21	108.7	C7—C8—C2	109.91 (8)
C2—C3—O4	108.31 (8)	C7—C8—O9	109.85 (8)
C2—C3—C5	108.81 (8)	C2—C8—O9	109.04 (8)
O4—C3—C5	109.40 (8)	C7—C8—H81	107.0
C2—C3—H31	108.9	C2—C8—H81	107.5
O4—C3—H31	111.0	O9—C8—H81	113.5
C5—C3—H31	110.3	C8—O9—H91	104.7
C3—O4—H41	110.7	C7—O10—H101	106.1
C3—C5—O6	111.36 (8)	C7—C11—O12	106.31 (8)
C3—C5—H51	111.1	C7—C11—H112	111.4
O6—C5—H51	105.1	O12—C11—H112	112.4
C3—C5—H52	107.7	C7—C11—H111	109.2
O6—C5—H52	110.4	O12—C11—H111	109.3
H51—C5—H52	111.2	H112—C11—H111	108.3
C5—O6—C7	114.34 (8)	C11—O12—H121	113.0

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H41...O10 ⁱ	0.81	2.02	2.8236 (14)	171
O9—H91...O1 ⁱⁱ	0.83	1.90	2.7203 (14)	173
O12—H121...O4 ⁱⁱⁱ	0.83	2.09	2.7875 (14)	142
O10—H101...O4 ^{iv}	0.81	2.10	2.8518 (14)	155
O1—H11...O6 ^v	0.81	1.96	2.7661 (14)	175

Symmetry codes: (i) $x, y+1, z$; (ii) $-x, y-1/2, -z+1/2$; (iii) $x+1, y-1, z$; (iv) $x+1/2, -y+1/2, -z$; (v) $x-1, y, z$.

Fig. 1

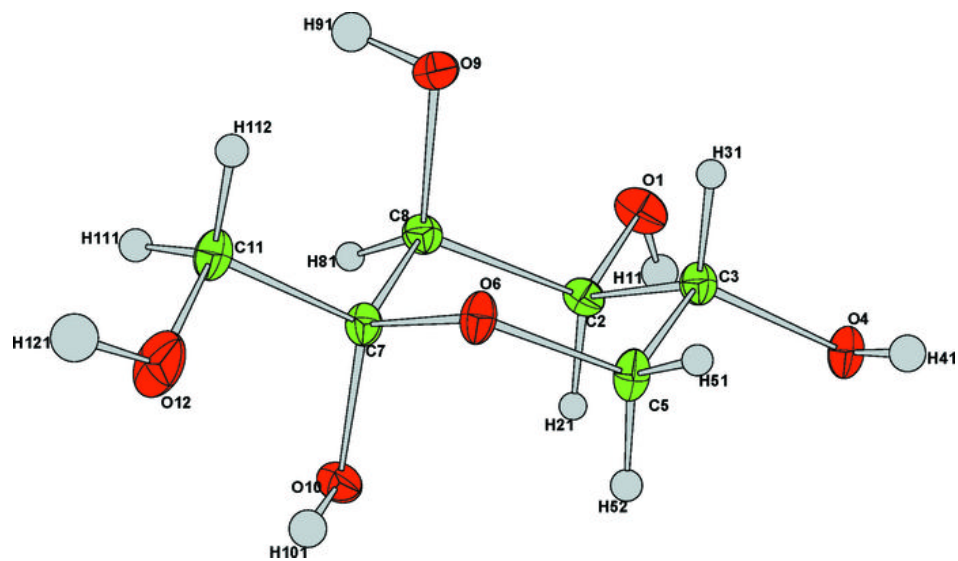


Fig. 2

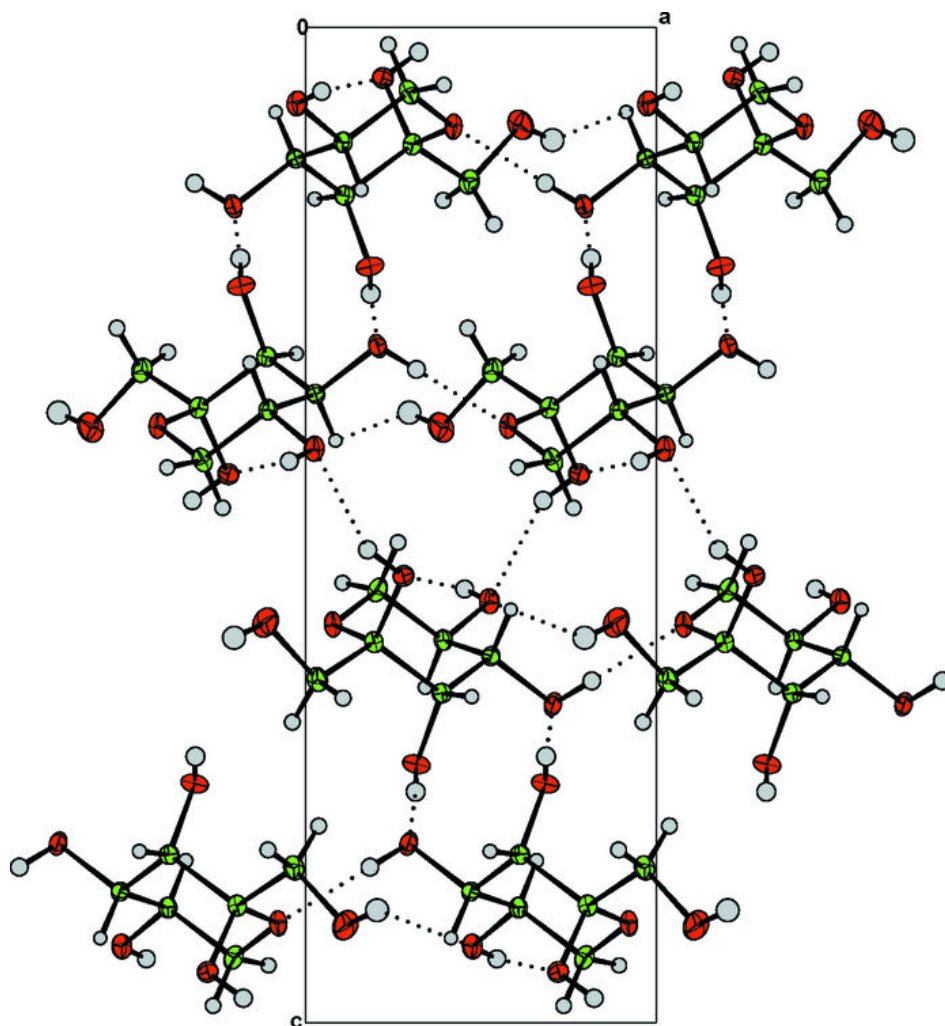


Fig. 3

