Acta Cryst. (1978). B**34**, 1873–1881

Conformation and Hydrogen Bonding of Disaccharides: The Crystal and Molecular Structure of Turanose [*O*-α-D-Glucopyranosyl-(1 → 3)-β-D-fructopyranose]

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(*Received* 5 *September* 1977; *accepted* 30 *October* 1977)

Turanose, $C_{12}H_{22}O_{11}$, is a disaccharide of α-D-glucose and β-D-fructose, linked α-1→3, with fructose as the reducing unit. Turanose is orthorhombic, space group $P2_12_12_1$, with $a = 8{\cdot}153$ (3), $b = 9{\cdot}205$ (2), $c = 19{\cdot}251$ (7) Å and $Z = 4$. The structure was solved by direct methods and refined to a final R of 0·031 for 1404 counter reflexions. The glucose ring has the usual $^4C_1$ pyranoside chair conformation. In contrast to all known fructose-containing oligosaccharides where the fructose moiety occurs in several variations of furanoside twist and envelope conformations, the fructose ring in turanose represents a unique case in that it adopts the $^2C_5$ pyranoside chair conformation of free β-D-fructose. The conformations about the exocyclic C–C bonds of the glucose and fructose units are *gauche–gauche* and *gauche–trans* respectively and differ from that of α-D-glucose (*gauche–trans*) and β-D-fructose (*gauche–gauche*). The conformation of the glycosidic α-1→3 linkage is analogous to that of the α-1→4 linkage of maltosides. Of the eight potential hydrogen-bond donors, one hydroxyl group does not act as a donor and another hydroxyl group interacts with an acceptor at a distance of 3·031 Å with O–H···O 134°, and should be considered as a weak interaction. Accordingly, the IR spectrum shows two sharp absorption maxima at frequencies near that of an unperturbed OH-group stretch vibration. One of the hydrogen bonds is intramolecular.

Introduction

Of the disaccharides belonging to the *O*-α-D-glucopyranosyl-(1→*X*)-D-fructose (X = 1, 2, 3, 4, 5, 6) family, the crystal structures of sucrose (X = 2) (Brown & Levy, 1973) and isomaltulose (X = 6) (Dreissig & Luger, 1973) have been determined. In these disaccharides as well as in the fructose-containing trisaccharides 1-kestose (Jeffrey & Park, 1972), two crystal modifications of melizitose (Hirotsu & Shimada, 1973; Avenel, Neuman & Gillier-Pandraud, 1976), raffinose (Berman, 1970), planteose (Rohrer, 1972) and the tetrasaccharide stachyose (Gilardi & Flippen, 1975), the fructose moiety occurs in several variations of the five-membered furanoside twist or envelope conformations. From synthetic (Stodola, Sharpe & Koepsell, 1956) and NMR experiments (van Heeswijk, Wassenburg & Vliegenthart, 1978) it has been shown that the fructose part of the disaccharide leucrose (X = 5) has the six-membered pyranose conformation which also occurs in crystalline β-D-fructose (Kanters, Roelofsen, Alblas & Meinders, 1977). However, this exceptional feature of leucrose is only apparent because the 1–5 glycosidic link simply imposes the six-membered pyranoside chair conformation. As part of our research programme on oligosaccharides we undertook the structure analyses of the disaccharides turanose (X = 3) and leucrose (X = 5). This paper describes the structure analysis of turanose with emphasis on conformation and hydrogen-bond pattern.

Experimental

Crystals of turanose were grown from a 1% aqueous ethanolic solution. Photographs showed that the crystal system is orthorhombic with space group $P2_12_12_1$. Accurate cell dimensions and intensities were measured

Table 1. *Crystal data for turanose*

Molecular formula	$C_{12}H_{22}O_{11}$
Formula weight	342·3
Crystal system	Orthorhombic
a (Å)	8·153 (3)
b (Å)	9·205 (2)
c (Å)	19·251 (7)
Systematic absences	$h00, h = 2n + 1$
	$0k0, k = 2n + 1$
	$00l, l = 2n + 1$
Space group	$P2_12_12_1$
V (Å^3)	1444·65
Z	4
D_x (g cm^{-3})	1·574
μ(Cu $K\alpha$) (cm^{-1})	12·38
Crystal dimensions (mm)	0·5 × 0·5 × 0·1
λ(Cu $K\alpha$) (Å)	1·54178

on an automatic Nonius CAD-3 diffractometer with Ni-filtered Cu $K\alpha$ radiation (λ = 1·54178 Å) with the ω-scan technique. The crystal data are summarized in Table 1. 1404 independent intensities were collected up to $\sin\theta/\lambda = 0{\cdot}64$ Å^{-1}; 110 reflexions with $I < 2{\cdot}5\sigma(I)$ were considered unobserved. After Lorentz–polarization corrections, a correction for absorption was applied (Coppens, 1970). The crystal shape was described by eight boundary planes and the absorption factors were in the range 1·12 to 1·48.

Determination and refinement of the structure

The structure was solved with *MULTAN* of the XRAY system (1972). The data were placed on an absolute scale by Wilson's (1942) method. For the structure determination 199 normalized structure factors with $|E| > 1{\cdot}4$ were used. The first E map revealed all non-hydrogen atoms. Isotropic block-diagonal least-squares refinement reduced R to 0·072.

A difference map revealed all 22 H atoms, with electron densities ranging from 0·25 to 0·56 e Å^{-3}. The positional parameters of the H atoms, with constant isotropic thermal parameters equal to those of the carrier atoms, were included in the refinement. Full-matrix least-squares refinement gave a final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}031$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0{\cdot}032$. The quantity minimized was $\Sigma w(F_o - F_c)^2$ with weights $w = \sigma^{-2}(F_o)$. In the last stage of the refinement an isotropic correction for secondary extinction was applied (Larson, 1967). The final value of g is $4{\cdot}1 \times 10^{-3}$. The goodness of fit is 2·24, the average shift/error ratio for all parameters is 0·10. A final difference synthesis showed no peaks above 0·15 e Å^{-3}. Scattering factors for C and O were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Positional parameters are listed in Table 2.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33206 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

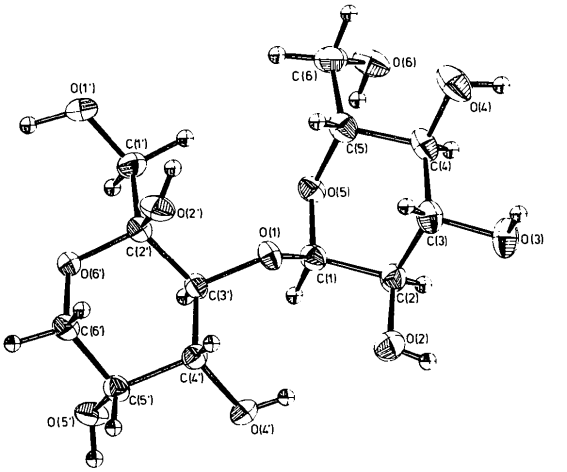


Fig. 1. Molecular conformation and atomic numbering of turanose. The glucose and fructose moieties are denoted by unprimed and single-primed designators respectively.

Table 2. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *for turanose*

The estimated standard deviations are given in parentheses and refer to the last decimal position of respective values.

	x	y	z		x	y	z
C(1)	829 (3)	4496 (3)	2634 (1)	H(C1)	0 (4)	369 (3)	253 (1)
C(2)	344 (3)	5235 (3)	3316 (1)	H(C2)	19 (3)	452 (3)	367 (1)
C(3)	1694 (4)	6216 (3)	3576 (1)	H(C3)	193 (3)	697 (3)	328 (1)
C(4)	3289 (4)	5358 (3)	3628 (1)	H(C4)	317 (3)	454 (3)	396 (1)
C(5)	3706 (4)	4690 (3)	2927 (1)	H(C5)	384 (3)	559 (3)	259 (1)
C(6)	5198 (4)	3728 (3)	2921 (1)	H(C6)	532 (3)	338 (3)	245 (1)
O(1)	890 (2)	5575 (2)	2111 (1)	H'(C6)	620 (4)	423 (3)	305 (1)
O(2)	−1154 (3)	6002 (2)	3187 (1)	H(O2)	−151 (3)	619 (3)	353 (1)
O(3)	1192 (3)	6765 (2)	4237 (1)	H(O3)	172 (3)	766 (3)	427 (1)
O(4)	4620 (3)	6276 (2)	3833 (1)	H(O4)	456 (3)	639 (3)	427 (1)
O(5)	2356 (2)	3793 (2)	2704 (1)	H(O6)	431 (3)	210 (3)	333 (1)
O(6)	5105 (2)	2585 (2)	3421 (1)	H(C1')	248 (3)	337 (3)	85 (1)
C(1')	2960 (3)	4440 (3)	929 (1)	H'(C1')	353 (3)	465 (3)	142 (1)
C(2')	1524 (3)	5494 (3)	879 (1)	H(C3')	1 (3)	405 (3)	145 (1)
C(3')	238 (3)	5166 (3)	1444 (1)	H(C4')	−104 (3)	709 (3)	138 (1)
C(4')	−1321 (3)	6025 (3)	1326 (1)	H(C5')	−286 (3)	641 (3)	49 (1)
C(5')	−1994 (3)	5798 (3)	594 (1)	H(C6')	−25 (3)	710 (3)	15 (1)
C(6')	−630 (3)	6125 (3)	88 (1)	H'(C6')	−97 (3)	591 (3)	−40 (1)
O(1')	4200 (2)	4740 (2)	431 (1)	H(O1')	388 (3)	412 (3)	−2 (1)
O(2')	1996 (2)	6954 (2)	909 (1)	H(O2')	288 (3)	698 (3)	106 (1)
O(4')	−2552 (2)	5641 (2)	1822 (1)	H(O4')	−224 (3)	596 (3)	219 (1)
O(5')	−2546 (2)	4343 (2)	496 (1)	H(O5')	−355 (3)	436 (3)	51 (1)
O(6')	782 (2)	5230 (2)	223 (1)				

Table 3. *Bond distances* (Å) *involving non-hydrogen atoms with corresponding values for* α-D-*glucose and* β-D-*fructose*

The e.s.d.'s are given in parentheses.

	Turanose[a] glucose moiety	α-D-Glucose[b]		Turanose[a] fructose moiety	β-D-Fructose[c]
C(1)–C(2)	1·530 (4)	1·534	C(1′)–C(2′)	1·523 (4)	1·520 (4)
C(2)–C(3)	1·509 (4)	1·525	C(2′)–C(3′)	1·540 (4)	1·540 (4)
C(3)–C(4)	1·525 (4)	1·519	C(3′)–C(4′)	1·514 (4)	1·518 (4)
C(4)–C(5)	1·522 (4)	1·528	C(4′)–C(5′)	1·525 (4)	1·524 (4)
C(1)–O(5)	1·410 (3)	1·426	C(5′)–C(6′)	1·509 (4)	1·494 (5)
C(5)–O(5)	1·441 (3)	1·427	C(6′)–O(6′)	1·439 (3)	1·436 (4)
C(5)–C(6)	1·505 (4)	1·510	C(2′)–O(6′)	1·422 (3)	1·413 (3)
C(6)–O(6)	1·428 (4)	1·413	C(1′)–O(1′)	1·421 (3)	1·422 (4)
C(1)–O(1)	1·416 (3)	1·389	C(2′)–O(2′)	1·400 (3)	1·411 (4)
C(2)–O(2)	1·432 (3)	1·415	C(3′)–O(1)	1·441 (3)	1·425 (4)
C(3)–O(3)	1·429 (3)	1·415	C(4′)–O(4′)	1·431 (3)	1·415 (4)
C(4)–O(4)	1·430 (4)	1·425	C(5′)–O(5′)	1·425 (3)	1·423 (4)

References: (*a*) This article. (*b*) Brown & Levy (1965). (*c*) Kanters, Roelofsen, Alblas & Meinders (1977).

Description of the structure

The conformation of the molecule and the numbering of the atoms are shown in Fig. 1. The glucose and fructose moieties are denoted by unprimed and single-primed designators respectively.

In turanose the D-glucose moiety has the usual $^4C_1$ pyranoside chair conformation. However, the fructose moiety has the six-membered $^2C_5$ chair conformation. Turanose therefore represents a unique case, because of the known preference (see *Introduction*) for the furanoside conformation of D-fructose in oligosaccharides. It is interesting to note that D-fructose in the turanose moiety of both crystal modifications of the trisaccharide melizitose (Hirotsu & Shimada, 1973; Avenel, Neuman & Gillier-Pandraud, 1976) has the five-membered furanoside form.

Bond distances

In Table 3 bond distances involving C and O atoms are compared with those of the constituent monosaccharides α-D-glucose (Brown & Levy, 1965) and β-D-fructose (Kanters, Roelofsen, Alblas & Meinders, 1977).

The C–C bonds range from 1·505 to 1·540 Å (mean 1·520 Å). Exocyclic C(5)–C(6) (1·505 Å) and endocyclic C(5′)–C(6′) (1·509 Å) are short, in agreement with the corresponding bond lengths of α-D-glucose and β-D-fructose (Table 3).

The exocyclic C–O bonds range from 1·400 to 1·441 Å (mean 1·425 Å). The anomeric C(2′)–O(2′) distance is short (1·400 Å) and differs by 8σ from the mean.

The endocyclic C–O bonds range from 1·410 to 1·441 Å (mean 1·428 Å). Of the two anomeric C–O bonds, C(1)–O(1) and C(2′)–O(2′), the former is part of the glycosidic 1–3 link whereas the latter is free. Berman, Chu & Jeffrey (1967) have pointed out that in the axial series the shortening of anomeric C–O bonds in glycosides is smaller and the disproportionation of endocyclic C–O bonds more striking. In accordance with this, the glycosidic C(1)–O(1) is 1·416 Å and free C(2′)–O(2′) 1·400 Å and the pairs of endocyclic C–O bonds C(1)–O(5), C(5)–O(5) and C(2′)–O(6′), C(6′)–O(6′) are 1·410, 1·441 and 1·422, 1·439 Å respectively.

The average length of the 14 C–H bonds is 1·00 (5) Å, that of the 8 O–H bonds 0·85 (11) Å.

Bond angles

In Table 4 bond angles involving C and O atoms are compared with the corresponding angles of α-D-glucose (Brown & Levy, 1965) and β-D-fructose (Kanters, Roelofsen, Alblas & Meinders, 1977).

The internal C–C–C angles range from 107·6 to 111·6° (mean 110·2°), the exocyclic C–C–O angles range from 107·0 to 113·4° (mean 110·2°). Both means are close to tetrahedral.

The C–O–C bridge angle in turanose is 116·0° and agrees with bridge angles of oligosaccharides with different types of linkages and methyl glycosides (Kanters, Roelofsen, Doesburg & Koops, 1976).

Bond angles involving H atoms have mean values distributed as follows over the different classes: H–C–C (21 contributors) 109; H–C–O (15) 108; H–O–C (8) 107; and H–C–H (3) 112°.

Table 4. *Bond angles* (°) *involving non-hydrogen atoms with corresponding values for* α-D-*glucose and* β-D-*fructose*

The e.s.d.'s for bond angles in turanose and β-D-fructose are 0·2°.

	Turanose[a] glucose moiety	α-D-Glucose[b]		Turanose[a] fructose moiety	β-D-Fructose[c]
C(1)–C(2)–C(3)	111·2	111·1	O(1′)–C(1′)–C(2′)	112·4	110·4
C(2)–C(3)–C(4)	109·5	109·8	C(1′)–C(2′)–C(3′)	110·8	112·3
C(3)–C(4)–C(5)	109·9	111·2	C(2′)–C(3′)–C(4′)	111·3	111·2
C(4)–C(5)–O(5)	109·0	108·7	C(3′)–C(4′)–C(5′)	111·6	109·3
C(5)–O(5)–C(1)	116·1	113·8	C(4′)–C(5′)–C(6′)	107·6	111·1
O(5)–C(1)–C(2)	110·5	110·1	C(5′)–C(6′)–O(6′)	111·0	111·0
O(5)–C(1)–O(1)	111·0	111·5	C(6′)–O(6′)–C(2′)	113·8	114·6
C(2)–C(1)–O(1)	107·9	109·4	O(6′)–C(2′)–C(3′)	107·7	111·2
C(1)–C(2)–O(2)	107·0	110·8	O(6′)–C(2′)–O(2′)	108·5	111·2
C(3)–C(2)–O(2)	112·6	112·3	C(3′)–C(2′)–O(2′)	110·3	106·8
C(2)–C(3)–O(3)	107·3	108·1	C(2′)–C(3′)–O(1)	109·1	111·1
C(4)–C(3)–O(3)	111·6	110·6	C(4′)–C(3′)–O(1)	107·9	108·8
C(3)–C(4)–O(4)	111·0	108·3	C(3′)–C(4′)–O(4′)	111·1	110·2
C(5)–C(4)–O(4)	108·3	110·9	C(5′)–C(4′)–O(4′)	109·3	109·6
C(4)–C(5)–C(6)	115·1	111·6	C(4′)–C(5′)–O(5′)	111·4	110·8
O(5)–C(5)–C(6)	106·1	108·1	C(6′)–C(5′)–O(5′)	109·6	107·3
C(5)–C(6)–O(6)	112·7	110·4	C(1′)–C(2′)–O(2′)	113·4	110·8
Bridge C(1)–O(1)–C(3′)	116·0		C(1′)–C(2′)–O(6′)	105·9	104·6

References: (*a*) This article. (*b*) Brown & Levy (1965). (*c*) Kanters, Roelofsen, Alblas & Meinders (1977).

Molecular conformation

The endo- and exocyclic torsion angles of turanose with corresponding angles of α-D-glucose (Brown & Levy, 1965) and β-D-fructose (Kanters, Roelofsen, Alblas & Meinders, 1977) are given in Tables 5 and 6 respectively.

In turanose the mean endocyclic torsion angles of the glucose and fructose moieties are 56·0 and 57·3° respectively, the smallest values 52·8 and 53·3° and the largest values 57·0 and 64·3°. All torsion angles are within the ranges reported in previous tabulations (Arnott & Scott, 1972).

In glucosides the conformation about C(5)–C(6) is either *gauche–gauche* or *gauche–trans* (Sundaralingam, 1968; Longchambon, Ohannessian, Avenel & Neuman, 1975; Kanters, Roelofsen, Doesburg & Koops, 1976). In the glucose part of turanose the conformation about C(5)–C(6) is identical with that of β-D-glucose (*gauche–gauche*) (Chu & Jeffrey, 1968), but different from that of α-D-glucose where the conformation is *gauche–trans*.

The conformation about exocyclic C(1′)–C(2′) in the fructose moiety is *gauche–trans*, in β-D-fructose it is *gauche–gauche*. The differences in conformation angles about exocyclic C–C bonds show the rotational freedom of the primary alcohol groups. The *trans–gauche* conformation about exocyclic C–C bonds in saccharides seldom occurs (Sundaralingam, 1968), owing to the short O(6)···O(4) *peri* interaction. In the fructose part of turanose it is even more unfavourable because of the resulting very short intramolecular contact O(1′)···O(5) (2·59 Å).

Table 5. *Endocyclic torsion angles* (°) *of turanose,* α-D-*glucose and* β-D-*fructose*

The torsion angle $A(1)$–$A(2)$–$A(3)$–$A(4)$ is viewed along $A(2)$–$A(3)$, with a clockwise rotation of $A(1)$ to $A(4)$ taken to be positive.

	Turanose[a] glucose moiety	α-D-Glucose[b]
O(5)–C(1)–C(2)–C(3)	52·8	54·1
C(1)–C(2)–C(3)–C(4)	−54·2	−51·2
C(2)–C(3)–C(4)–C(5)	56·7	53·3
C(3)–C(4)–C(5)–O(5)	−57·0	−57·5
C(4)–C(5)–O(5)–C(1)	58·8	62·2
C(5)–O(5)–C(1)–C(2)	−56·3	−61·0
Average	56·0	56·6

	Turanose[a] fructose moiety	β-D-Fructose[c]
O(6′)–C(2′)–C(3′)–C(4′)	−54·8	−52·7
C(2′)–C(3′)–C(4′)–C(5′)	53·7	52·2
C(3′)–C(4′)–C(5′)–C(6′)	−53·3	−54·7
C(4′)–C(5′)–C(6′)–O(6′)	57·0	56·5
C(5′)–C(6′)–O(6′)–C(2′)	−64·3	−58·0
C(6′)–O(6′)–C(2′)–C(3′)	60·6	55·6
Average	57·3	55·0

References: (*a*) This article. (*b*) Brown & Levy (1965). (*c*) Kanters, Roelofsen, Alblas & Meinders (1977).

The differences in ring torsion angles in the glucose and fructose parts of turanose and the constituent

Table 6. *Exocyclic torsion angles* (°) *of turanose,* α-D-*glucose and* β-D-*fructose*

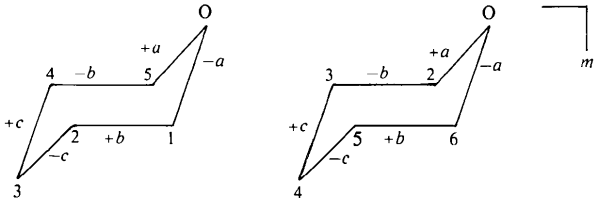
	Turanose[a] glucose moiety	α-D-Glucose[b]		Turanose[a] fructose moiety	β-D-Fructose[c]
O(5)–C(1)–C(2)–O(2)	176·1	179·7	O(1′)–C(1′)–C(2′)–C(3′)	−177·9	58·4
O(1)–C(1)–C(2)–C(3)	−68·8	−68·8	O(1′)–C(1′)–C(2′)–O(2′)	−53·3	177·7
O(1)–C(1)–C(2)–O(2)	54·5	56·8	O(1′)–C(1′)–C(2′)–O(6′)	65·5	−62·4
C(1)–C(2)–C(3)–O(3)	−175·5	−172·0	C(1′)–C(2′)–C(3′)–C(4′)	−170·2	−169·6
O(2)–C(2)–C(3)–C(4)	−174·2	−176·0	C(1′)–C(2′)–C(3′)–O(1)	70·9	69·1
O(2)–C(2)–C(3)–O(3)	64·5	63·2	O(2′)–C(2′)–C(3′)–C(4′)	63·4	68·8
C(2)–C(3)–C(4)–O(4)	176·5	175·4	O(2′)–C(2′)–C(3′)–O(1)	−55·5	−52·5
O(3)–C(3)–C(4)–C(5)	175·4	172·5	O(6′)–C(2′)–C(3′)–O(1)	−173·7	−174·0
O(3)–C(3)–C(4)–O(4)	−64·8	−65·4	C(2′)–C(3′)–C(4′)–O(4′)	175·9	172·7
C(3)–C(4)–C(5)–C(6)	−176·1	−176·6	O(1)–C(3′)–C(4′)–C(5′)	173·3	174·9
O(4)–C(4)–C(5)–O(5)	−178·4	−178·1	O(1)–C(3′)–C(4′)–O(4′)	−64·5	−64·7
O(4)–C(4)–C(5)–C(6)	62·5	62·9	C(3′)–C(4′)–C(5′)–O(5′)	66·8	64·5
C(6)–C(5)–O(5)–C(1)	−176·7	−176·5	O(4′)–C(4′)–C(5′)–C(6′)	−176·6	−175·5
C(5)–O(5)–C(1)–O(1)	63·4	60·6	O(4′)–C(4′)–C(5′)–O(5′)	−56·4	−56·3
O(5)–C(5)–C(6)–O(6)	−65·3	70·3	O(5′)–C(5′)–C(6′)–O(6′)	−64·3	−64·8
C(4)–C(5)–C(6)–O(6)	55·3	−170·3	C(1′)–C(2′)–O(6′)–C(6′)	179·2	177·1
			O(2′)–C(2′)–O(6′)–C(6′)	−58·8	−63·3

References: (*a*) This article. (*b*) Brown & Levy (1965). (*c*) Kanters, Roelofsen, Alblas & Meinders (1977).

Table 7. *Mean values of ring torsion angles* (°) *and ring-puckering parameter* θ (°) *(Cremer & Pople,* 1975*) of turanose,* α-D-*glucose and* β-D-*fructose*

Δ, ⟨Δ⟩ are maximum and mean differences between mirror-related torsion angles.

	⟨*a*⟩	⟨*b*⟩	⟨*c*⟩	Δ	⟨Δ⟩	θ
Turanose[i]						
glucose moiety	57·6	54·9	55·4	4·6	3·1	4·3
fructose moiety	62·4	55·9	53·5	3·1	2·1	2·9
α-D-Glucose[ii]	61·6	55·8	52·2	3·4	2·3	3·5
β-D-Fructose[iii]	56·8	54·6	53·4	4·3	2·9	2·6



Glucose Fructose

References: (i) This article. (ii) Brown & Levy (1965). (iii) Kanters, Roelofsen, Alblas & Meinders (1977).

Table 8. *Torsion angles* (°) *involving hydrogen atoms in turanose*

	Glucose moiety		Fructose moiety
H(C1)···H(C2)*	52·1	H(C3′)···H(C4′)	174·2
H(C2)···H(C3)	−178·3	H(C4′)···H(C5′)	−54·1
H(C3)···H(C4)	177·1	H(C5′)···H(C6′)	62·6
H(C4)···H(C5)	−179·4	H(C5′)···H′(C6′)	−63·4
H(C5)···H(C6)	−60·8	H(C1′)···H(O1′)	29·3
H(C5)···H′(C6)	58·2	H′(C1′)···H(O1′)	155·4
H(C2)···H(O2)†	45·2	H(C4′)···H(O4′)	−48·2
H(C3)···H(O3)	−27·7	H(C5′)···H(O5′)	−20·2
H(C4)···H(O4)	−43·1		
H(C6)···H(O6)	−61·7		
H′(C6)···H(O6)	−178·0		

* Refers to the torsion angle H(C1)–C(1)–C(2)–H(C2).
† Refers to the torsion angle H(C2)–C(2)–O(2)–H(O2).

monosaccharides (Table 5) reveal that the conformation of the pyranose ring does not change appreciably on formation of a disaccharide and hence must be very rigid. As has already been reported (Arnott & Scott, 1972; Jeffrey, McMullan & Takagi, 1977), pyranose rings in monosaccharides have approximate mirror symmetry normal to the mean plane of the ring and passing through ring O(5) and C(3) atoms of aldohexoses [O(6) and C(4) of ketohexoses] with more puckering at O and less puckering at C. Table 7 shows that the deviations from mirror symmetry of both rings of turanose are small and of the same order as in the constituting monosaccharides and also that there is an excellent agreement with the distortion derived from the puckering parameter θ defined by Cremer & Pople (1975). Deviations from mirror symmetry arise from the asymmetric distribution of ring substituents and from the difference in endocyclic C–O bond lengths due to the anomeric effect (Jeffrey, McMullan & Takagi, 1977).

The H atoms on neighbouring C atoms of the pyranose rings may be in *trans* (180°) or *gauche* (60°) orientations. The deviation of H–C–C–H torsion angles (Table 8) from these ideal arrangements is small;

the deviation of the H–C–O–H torsion angles, involving OH groups attached to ring C atoms, from the preferred *gauche* conformation (Sundaralingam, 1968) undoubtedly relates to the participation of the OH groups in hydrogen bonding and to other inter- and intramolecular interactions.

The conformation of the interglycosidic linkage is important in determining the conformation of disaccharide molecules. This conformation depends on the type of linkage between the sugar residues. The structures of several members of the class of 1→4 linked pyranoside disaccharides in which C(1)–O(1) is either equatorial (*e*) or axial (*a*) are known. The four torsion angles about the glycosidic C–O bonds of the 1*e*,4*e*-disaccharides β-cellobiose (Chu & Jeffrey, 1968), α-lactose (Fries, Rao & Sundaralingam, 1971), β-lactose (Hirotsu & Shimada, 1974) and methyl β-cellobioside (Ham & Williams, 1970) show a larger deviation from the values of the ideal fully extended (straight backbone) conformation (±120°) than those of the 1*a*,4*e*-disaccharides β-maltose (Quigley, Sarko & Marchessault, 1970), methyl β-maltopyranoside (Chu & Jeffrey, 1967) and phenyl α-maltoside (Tanaka, Tanaka, Ashida & Kakudo, 1976). The average deviation of the 1*e*,4*e* types is about 30° (Hirotsu & Shimada, 1974), that of the 1*a*,4*e* types only about 11° (Table 9).

Table 9. *Torsion angles* (°) *of the glycosidic linkage of turanose and some related disaccharides*

The Sundaralingam (1968) torsion angles are defined as φ_1 O(5)–C(1)–O(1)–C(4′); φ_1' C(2)–C(1)–O(1)–C(4′); φ_2 C(1)–O(1)–C(4′)–C(3′) and φ_2' C(1)–O(1)–C(4′)–C(5′) for 1*a*,4*e* maltosides, and for turanose as φ_1 O(5)–C(1)–O(1)–C(3′); φ_1' C(2)–C(1)–O(1)–C(3′); φ_2 C(1)–O(1)–C(3′)–C(4′) and φ_2' C(1)–O(1)–C(3′)–C(2′). The torsion angle *A*(1)–*A*(2)–*A*(3)–*A*(4) is viewed along *A*(2)–*A*(3), with a clockwise rotation of *A*(1) to *A*(4) taken to be positive.

	Turanose[a]	Phenyl α-maltoside[b]		Methyl β-maltoside[c]	β-Maltose[d]
φ_1	99·2	110·0	108·5	110·0	123·1
φ_1'	−139·6	−129·0	−128·8	−128·2	−116·6
φ_2	111·2	100·3	102·2	129·2	132·4
φ_2'	−127·8	−138·9	−139·4	−108·9	−109·7

References: (*a*) This article. (*b*) Tanaka, Tanaka, Ashida & Kakudo (1976). (*c*) Chu & Jeffrey (1967). (*d*) Quigley, Sarko & Marchessault (1970).

The principal factors which cause these deviations are relaxation of the non-bonded interaction between H(C) atoms of the linkage and, more important, the connexion between the pyranose rings formed by an intramolecular hydrogen bond which is invariably present in these compounds. The larger deviation of the torsion angles of 1*e*,4*e*-disaccharides relates to the fact that here the intramolecular hydrogen bond involves a OH group and a ring O atom, whereas in the 1*a*,4*e*-disaccharides the bond is between two OH groups.

As a consequence the donor–acceptor separation of 1*e*,4*e*-glycosides in the theoretical fully extended conformation has a calculated average of about 3·6 Å, whereas the separation of the 1*a*,4*e*-glycosides in the ideal situation will be about 2·5 Å. It follows that formation of an intramolecular hydrogen bond in the 1*e*,4*e* types demands larger rotations about the glycosidic C–O bonds than in the 1*a*,4*e* types. In the latter types the rotation mainly serves to force the donor and acceptor further apart to distances that are associated with hydrogen bonds between aliphatic OH groups (2·65–2·90 Å) (Kroon, Kanters, van Duijneveldt-van de Rijdt, van Duijneveldt & Vliegenthart, 1975).

Though the glycosidic linkage in turanose is 1*a*,3*e*, it turns out to be analogous to that of the 1*a*,4*e*-disaccharides; this is because turanose is composed of an aldohexose *C*1 and a ketohexose 1*C* chair. The analogy is borne out by comparison of the torsion angles (Table 9) of turanose with those of the 1*a*,4*e*-

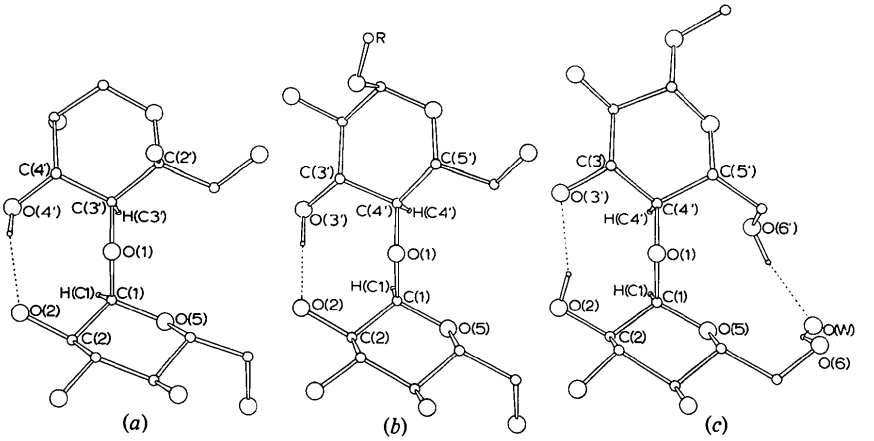


Fig. 2. Views of (*a*) turanose, and (*b*) phenyl α-maltoside (*R* = phenyl) and (*c*) methyl β-maltoside, two 1*a*,4*e*-disaccharides, along the bisector of the glycosidic angle C–O–C. (Of phenyl α-maltoside only independent molecule *A* is shown.)

disaccharides. This analogy is visualized in Fig. 2, which shows a view of the structures of turanose and some 1*a*,4*e*-disaccharides along the bisector of the glycosidic C–O–C linkage. Inspection of the torsion angles in Table 9 also reveals that the conformations of turanose and the two independent molecules of phenyl α-maltoside result from rotations about the C–O bonds in the same direction, yielding a less extended conformation, whereas the rotations in methyl β-maltopyranoside are opposite, keeping the conformation as extended as possible. In the former case the H(C) atoms are at opposite sides of the C–O–C linkage, in the latter case at the same side (Fig. 2).

β-Maltose represents an exception in that φ_1 is >120° (Table 9). The significance of it is difficult to assess because of uncertainty in the structural parameters owing to the poor quality of the crystal (Quigley, Sarko & Marchessault, 1970).

The difference in conformation between turanose and phenyl α-maltoside on the one hand and methyl β-maltopyranoside on the other may well be explained by the presence of a water molecule in the structure of the latter compound. This water molecule serves as acceptor for both side-chain OH groups, thus constituting another (pseudo)intramolecular hydrogen bond at the alternate side of the molecule (Fig. 2). The water molecule giving rise to a different intermolecular hydrogen-bond scheme possibly accounts for the opposite donor–acceptor direction of the intramolecular hydrogen bond (Fig. 2).

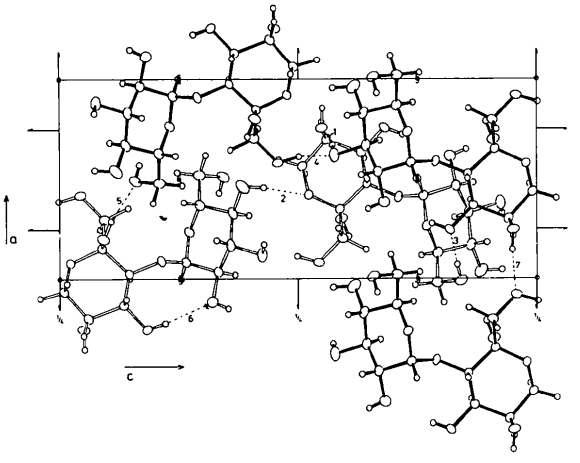


Fig. 3. A view of the molecular packing and hydrogen bonds of turanose seen along **b**. Hydrogen bonds, numbered according to Table 10, are indicated by dashed lines.

Hydrogen bonding

Of the eight potential hydrogen-bond donors, O(2)–H(O2) is not a donor. Two O–H groups, O(4)–H(O4) and O(2′)–H(O2′), do not act as acceptors, whereas only ring O atom O(6′) accepts a hydrogen bond. In contrast to many known cases (Sundaralingam, 1968) in which the hydrogen bond to a ring O atom of a pyranose system is equatorially oriented at the acceptor O atom, the orientation in turanose is neither equatorial nor axial, but about halfway between. This follows from the torsion angles H(O4)···O(6′)–C(2′)–C(3′) and H(O4)···O(6′)–C(6′)–C(5′), −100 and 105° respectively. So far, a similar orientation has been observed in α,α-trehalose (Brown, Rohrer, Berking, Beevers, Gould & Simpson, 1972). As usual, glycosidic O(1) is not an acceptor.

In Fig. 3, which shows a projection of the structure down **b**, the seven hydrogen bonds are indicated and their geometry is given in Table 10. Of the two hydrogen-bond sequences, one is a three-membered infinite donor–acceptor chain O(3)→O(5′)→O(1′)→O(3) winding along the **a** direction and the other, running along **b**, consists of three hydrogen bonds, O(2′)→O(6)→O(4′)→O(2). The latter is finite, not because it ends at a ring O acceptor, as is commonly seen in saccharide structures, but because O(2) has neither inter- nor intramolecular contacts with acceptable O–H···O geometry (O···O < 3·60 Å *and*

Table 10. *Geometry of the hydrogen bonds in turanose*

Bond No.		O–H	H···O	O···O	O–H···O	Symmetry operation*
1	O(3)–H(O3)···O(5′)	0·93 (3) Å	1·75 (3) Å	2·668 (3) Å	169 (3)°	555.4
2	O(4)–H(O4)···O(6′)	0·84	2·39	3·031	134	565.2
3	O(6)–H(O6)···O(4′)	0·80	1·99	2·784	170	545.4
4	O(1′)–H(O1′)···O(3)	1·07	1·65	2·702	167	564.2
5	O(2′)–H(O2′)···O(6)	0·78	2·00	2·754	163	655.4
6	O(4′)–H(O4′)···O(2)	0·81	2·11	2·884	159	555.1
7	O(5′)–H(O5′)···O(1′)	0·82	1·87	2·681	168	455.1

* The symmetry operation is performed on the acceptor O atoms. The first set of numbers specifies the lattice translations, *e.g.* 645.4 is +**a** − **b** from 555.4. The last digit indicates one of the following symmetry operations: (1) x,y,z; (2) $\frac{1}{2}-x,-y,\frac{1}{2}+z$; (3) $\frac{1}{2}+x,\frac{1}{2}-y,-z$; (4) $-x,\frac{1}{2}+y,\frac{1}{2}-z$.

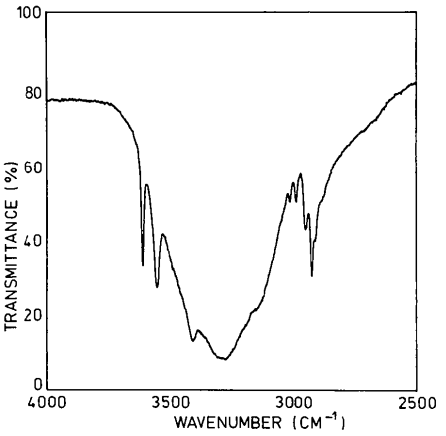


Fig. 4. IR spectrum of the region 2500–4000 cm^{-1} of turanose in a KBr pellet.

O—H···O > 120°). This feature is unique in structures of (oligo)saccharides in which molecular packing and rotational flexibility of the C—O—H group nearly always enable the realization of O—H···O contacts with geometries that are within the ranges that are considered normal for hydrogen bonds.

In previous work (Kanters, Kroon, Peerdeman & Vliegenthart, 1969; Kanters, Roelofsen, Alblas & Meinders, 1977) we showed that inspection of the IR O—H stretching vibration (3000–3600 cm^{-1}) can be very helpful in depicting O—H···O interactions as hydrogen bonds. As can be seen in Fig. 4 the IR spectrum of turanose contains two sharp absorption peaks at 3610 and 3550 cm^{-1}. The free, unperturbed O—H group has a stretching vibration absorbing at about 3600 cm^{-1} (Coggeshall & Saier, 1951; Wilmshurst, 1956; Joesten & Schaad, 1974), so the turanose spectrum corroborates the finding that one of the O—H groups [O(2)—H(O2)] is not a hydrogen-bond donor. The second absorption peak at lower wavenumber indicates the presence of a weak hydrogen-bond interaction. Evidently, this peak corresponds to the O(4)—H(O4)···O(6′) hydrogen bond with O···O and O—H···O 3·031 Å and 134° respectively, all other hydrogen bonds having geometries that are well within current ranges (Table 10). A similar situation is found in β-D-fructose where model calculations and IR spectroscopy both indicate the presence of a weak interaction in the hydrogen-bond pattern (Kanters, Roelofsen, Alblas & Meinders, 1977).

Note added in proof: Following acceptance of this paper, the results of a structure determination of turanose were published by Neuman, Avenel & Gillier-Pandraud (1978). The dimensions of the molecule in the two analyses agree well. The average differences of corresponding bond distances, bond angles and conformation angles are 0·004 Å, 0·3° and 0·3° respectively. {The maximum differences in these quantities are 0·015 Å [for C(5)—C(6)], 0·9° [for C(2′)—C(3′)—O(1)] and 0·8° [for O(2′)—C(2′)—C(3′)—O(1)]respectively.} The agreement in the hydrogen-bond geometries is also very good, as follows from the average differences of the H···O and O···O distances and O—H···O angles which are 0·08 Å, 0·009 Å and 4° respectively. {The maximum differences are 0·16 Å [for H(O1′)···O(3)], 0·018 Å [for O(5′)···O(1′)] and 7° [for O(4)—H(O4)···O(6′) and O(4′)—H(O4′)···O(2)] respectively.}

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The Crystal and Molecular Structure of Adenine Hydrobromide Hemihydrate, $C_5H_5N_5.HBr.\frac{1}{2}H_2O$

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(*Received* 31 *October* 1977; *accepted* 12 *December* 1977)

The crystal and molecular structure of the title compound has been determined from 972 observed three-dimensional data measured by a single-crystal automated X-ray diffractometer. The unit cell is monoclinic with $a = 9{\cdot}018$ (2), $b = 4{\cdot}845$ (2), $c = 19{\cdot}693$ (5) Å, $\beta = 112{\cdot}87$ (2)°, $V = 792{\cdot}9$ (3) Å^3 and contains four formula units. The space group is $P2/c$. The refinement of parameters has been carried out by the least-squares method in block-diagonal approximation. The final R value was 0·025. The adenine base is protonated at the N(1) site. The bond lengths and valence angles within the adenine cation are in good accord with the isomorphous structure of adenine hydrochloride hemihydrate and with other monoprotonated adenine bases.

Introduction

The crystal and molecular structure of adenine hydrobromide hemihydrate has been determined as part of a study of nucleic acids and their components. It is the aim of this programme to elucidate the transfer of energy and information in nucleic acids. Single crystals of the title compound represent a model suitable for the interpretation of optical measurements on polynucleotides, carried out at the Institute of Physics, Charles University, Praha.

Thematically, the present work is a continuation of the study of adenine derivatives (Langer & Huml, 1978). From the beginning of the study it has been assumed that the crystal and molecular structure of the title compound is similar to that of adenine hydrochloride hemihydrate, which was studied with two-dimensional data by Broomhead (1948) and Cochran (1951), and recently with three-dimensional data of considerably higher precision by Kistenmacher & Shigematsu (1974). Preliminary crystal data for the title compound were published by Moravcová (1975).

Experimental

Crystals of adenine hydrobromide hemihydrate used in this study were prepared by J. Zachová at the Institute of Physics, Charles University, Praha. The formula was verified by elemental analysis. The crystals were transparent, red-brown and very brittle.