Acta Cryst. (1977). B33, 3737–3743

Stereochemistry of Unsaturated Amino Sugars. II. The Crystal and Molecular Structures of Peracetylated 1,2-Dideoxy-D-*xylo*- and D-*ribo*-aldopyranoses, $C_{16}H_{21}O_9N$

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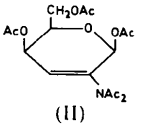
(*Received* 29 *April* 1977; *accepted* 28 *May* 1977)

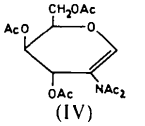
3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*xylo*-hex-1-enopyranose crystallizes in space group $P2_1$ with $a = 11{\cdot}466$, $b = 8{\cdot}126$, $c = 10{\cdot}019$ Å, $\beta = 103{\cdot}2°$, $Z = 2$. 3,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*ribo*-hex-1-enopyranose crystallizes in space group $P2_1$ with $a = 7{\cdot}963$, $b = 14{\cdot}741$, $c = 8{\cdot}447$ Å, $\beta = 113{\cdot}3°$, $Z = 2$. The structures were refined to an R of 0·046 for D-*xylo*- and 0·064 for D-*ribo*-aldopyranose. The sugar rings in both compounds exhibit the $^4H_5$ half-chair conformation: in the D-*ribo* isomer the conformation is symmetrical, in the D-*xylo* it is highly distorted. Owing to the absence of free hydroxyl groups, O—H···O hydrogen bonds are not possible. In the crystal the molecules are joined by van der Waals interactions only.

Introduction

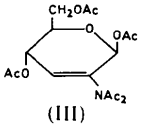
X-ray analysis of the first representative of a series of peracetylated unsaturated amino sugars (I, α-*threo*) was recently reported (Kojić-Prodić, Rogić & Ružić-Toroš, 1976). Two isomeric compounds from the same series, previously described as 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-β-D-*threo*-hex-2-enopyranose (II) and 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranose (III) (Pravdić, Židovec & Fletcher, 1973), are now found to be 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*xylo*-hex-1-enopyranose (IV) and 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*ribo*-hex-1-enopyranose (V) respectively.



(II)



(IV)



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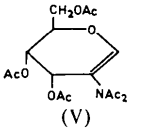
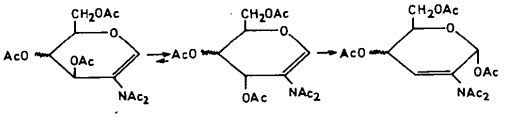


(V)

The assignment of structures II and III was made on the basis of the suggested mechanism for rearrangement which occurs in nucleophilic attack on acetylated glycals (Ferrier, Prasad & Sankey, 1968; Ferrier & Prasad, 1969). The structures proposed were in agreement with the reactivity and spectral characteristics (Pravdić, Židovec & Fletcher, 1973).

However, the fact that X-ray analysis established structures IV and V merits special comment on the formation of these two compounds. Isomerization of 3,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-1,2-dideoxy-D-*arabino*-hex-1-enopyranose (VI) through the action of acetic anhydride/$ZnCl_2$ gave 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranose (VII) as the major product (Pravdić, Židovec & Fletcher, 1970). Later, a minor component was isolated in the crystalline state, and proved to be an intermediate in the isomerization process (VI) → (VII) (Pravdić, Židovec & Fletcher, 1973). The same was valid in the isomerization of the isomeric compound from the D-*lyxo* series (VIII) into (I), where a corresponding intermediate was also found. As it is now evident that, in these reactions, the initial intermediates are the compounds of structure V and IV, respectively, the full process can be presented as follows.



D-*arabino* (VI) D-*ribo* (V) D-*erythro* (VII)
D-*lyxo* (VIII) D-*xylo* (IV) D-*threo* (I)

It seems reasonable to assume that this pathway proceeds through initial isomerization at C(3), and then by the attack of the C(3) acetoxy group at C(1) from the more accessible side, followed by allylic rearrangement of the double bond into the C(2)=C(3) position. The isomerization that takes place at C(3), although

rather unusual and unexpected, may be regarded as a consequence of the allylic activation of H(3) (DeWolfe & Young, 1956).

Experimental

Weissenberg photographs recorded with Cu $K\alpha$ radiation indicated $P2_1$ or $P2_1/m$ for both crystals. Since the molecules are optically active, the space group is necessarily $P2_1$ (Table 1).

The intensities were collected on a Philips PW 1100 computer-controlled diffractometer in the $\omega/2\theta$ scan mode with graphite-monochromated Mo $K\alpha$ radiation. 1753 independent observed reflexions of the D-*xylo*- and 2191 reflexions of the D-*ribo*-aldopyranose were recorded and only these were used in the calculations. The reflexions with $I < 2\sigma_I$ were treated as unobserved. Three standard reflexions measured every 2 h showed no significant variation. The data were corrected for background, Lorentz and polarization effects, and for monochromator polarization.

Structure determination and refinement

The structures were solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). An overall temperature factor [B = 1·97 (IV); B = 2·15 Å^2 (V)] and the scale factors were determined (Wilson, 1942) and used to compute normalized structure amplitudes. The solutions were based on 300 reflexions with $|E| >$ 1·3 in both cases. The E map corresponding to the solution with the best figure of merit revealed the positions of all non-hydrogen atoms (26) in the D-*xylo* compound. The E map selected on the basis of the same criterion located 23 non-hydrogen atoms in the D-*ribo* isomer. Three of the terminal methyl groups were determined from the resulting Fourier synthesis. Full-matrix least squares with unit weights were used for refinement. Heavy-atom coordinates, isotropic thermal

Table 1. *Crystallographic and physical data for* 3,4,6-*tri-O-acetyl*-2-(*N-acetylacetamido*)-1,2-*dideoxy*-D-*xylo-hex*-1-*enopyranose*, $C_{16}H_{21}O_9N$ (IV) *and* 3,4,6-*tri-O-acetyl*-2-(*N-acetylacetamido*)-1,2-*dideoxy*-D-*ribo-hex*-1-*enopyranose*, $C_{16}H_{21}O_9N$ (V)

Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digit.

	(IV)	(V)
FW	371·35	371·35
Space group	$P2_1$	$P2_1$
a (Å)	11·466 (5)	7·963 (2)
b (Å)	8·126 (4)	14·741 (5)
c (Å)	10·019 (5)	8·447 (4)
β (°)	103·2 (1)	113·3 (1)
U (Å^3)	933·50	991·53
Z	2	2
D_m (g cm^{-3})	1·357	1·355
D_c (g cm^{-3})	1·357	1·346
μ(Mo $K\alpha$) (cm^{-1})	1·2	1·2
Crystal shape	Plate	Prism
Crystal dimensions (mm)	0·29×0·28×0·27	0·30×0·34×0·26

Table 2. *Final atomic positional parameters* (×10^4) *for non-hydrogen atoms of the* D-*xylo isomer* (IV)

	x	y	z
C(1)	5728 (3)	2691 (0)	5296 (4)
C(2)	6119 (3)	2928 (0)	4185 (4)
C(3)	7402 (3)	2685 (6)	4151 (4)
C(4)	8162 (3)	2724 (6)	5626 (4)
C(5)	7604 (4)	1608 (6)	6517 (5)
C(6)	8242 (4)	1634 (7)	8019 (5)
C(7)	5605 (4)	5158 (7)	2570 (5)
C(8)	5101 (5)	5712 (9)	1127 (5)
C(9)	4359 (4)	2612 (7)	2226 (5)
C(10)	4360 (5)	808 (8)	2565 (5)
C(11)	7533 (4)	899 (7)	2284 (4)
C(12)	7936 (5)	−777 (8)	1956 (6)
C(13)	8874 (4)	5475 (7)	5713 (5)
C(14)	8745 (6)	7152 (8)	6291 (7)
C(15)	10185 (4)	884 (9)	9251 (5)
C(16)	11369 (5)	234 (9)	9133 (6)
O(0)	6383 (2)	2093 (5)	6505 (3)
O(1)	6297 (3)	5980 (5)	3392 (3)
O(2)	3574 (3)	3208 (6)	1360 (4)
O(3)	7623 (3)	1052 (5)	3650 (3)
O(4)	7154 (4)	1981 (6)	1482 (4)
O(5)	8165 (2)	4371 (5)	6160 (3)
O(6)	9494 (3)	5133 (6)	4942 (4)
O(7)	9427 (3)	1011 (5)	8042 (3)
O(8)	9912 (4)	1281 (9)	10281 (4)
N	5318 (3)	3555 (5)	2969 (4)

Table 3. *Positional* (×10^3) *and isotropic thermal parameters* (Å^2 ×10^2) *for the hydrogen atoms of the* D-*xylo isomer* (IV)

	x	y	z	U
H(1)	492	285	533	3·7
H(3)	770	344	366	3·2
H(4)	898	241	566	3·0
H(5)	758	39	616	3·3
H(6,1)	784	103	857	4·1
H(6,2)	829	272	843	4·1
H(8,1)	421	631	106	5·8
H(8,2)	498	489	55	5·8
H(8,3)	565	640	88	5·8
H(10,1)	440	60	340	5·3
H(10,2)	500	20	220	5·3
H(10,3)	350	20	200	5·3
H(12,1)	870	−110	250	6·4
H(12,2)	790	−90	90	6·4
H(12,3)	740	−150	220	6·4
H(14,1)	788	750	580	6·7
H(14,2)	940	775	600	6·7
H(14,3)	880	720	720	6·7
H(16,1)	1200	110	980	6·4
H(16,2)	1152	−83	940	6·4
H(16,3)	1140	50	830	6·4

Table 4. *Final atomic positional parameters* ($\times 10^4$) *for non-hydrogen atoms of the* D-*ribo isomer* (V)

	x	*y*	*z*
C(1)	6977 (10)	442 (0)	10789 (11)
C(2)	5755 (10)	747 (0)	9271 (10)
C(3)	5946 (9)	1612 (5)	8445 (9)
C(4)	7440 (11)	2173 (5)	9778 (11)
C(5)	9105 (10)	1564 (6)	10692 (11)
C(6)	10825 (12)	2028 (7)	11895 (12)
C(7)	2534 (11)	500 (7)	8494 (12)
C(8)	749 (13)	42 (9)	7443 (17)
C(9)	4320 (13)	−622 (7)	7548 (13)
C(10)	6202 (15)	−858 (8)	7624 (18)
C(11)	5833 (12)	1918 (7)	5604 (11)
C(12)	6321 (16)	1540 (10)	4183 (13)
C(13)	6951 (15)	3650 (6)	8539 (13)
C(14)	7680 (21)	4333 (8)	7665 (17)
C(15)	11065 (13)	2227 (8)	14802 (13)
C(16)	10816 (18)	2896 (12)	16022 (16)
O(0)	8600 (8)	895 (4)	11678 (8)
O(1)	2614 (9)	1144 (6)	9399 (10)
O(2)	3059 (11)	−1110 (6)	6844 (14)
O(3)	6468 (8)	1372 (4)	7019 (7)
O(4)	4983 (11)	2592 (5)	5513 (9)
O(5)	8036 (8)	2898 (4)	8983 (8)
O(6)	5617 (11)	3726 (5)	8855 (11)
O(7)	10499 (9)	2569 (5)	3154 (8)
O(8)	11680 (11)	1475 (6)	15152 (10)
N	4175 (8)	186 (5)	8393 (9)

Table 5. *Positional parameters* ($\times 10^3$) *and isotropic thermal parameters* ($Å^2 \times 10^2$) *for the hydrogen atoms of the* D-*ribo isomer* (IV)

	x	*y*	*z*	*U*
H(1)	671	−15	1163	2·9
H(3)	461	193	814	2·4
H(4)	720	250	1060	2·8
H(5)	960	130	960	2·9
H(6,1)	1190	150	1230	3·4
H(6,2)	1110	238	1100	3·4

parameters and a scale factor were refined to R 0·107 for D-*xylo*- and 0·111 for D-*ribo*-aldopyranose. Anisotropic refinement (R = 0·068) and a subsequent difference synthesis located the H atoms in D-*xylo*-aldopyranose. Anisotropic refinement of parameters for the D-*ribo* compound led to an R of 0·075, but a subsequent difference synthesis revealed only the H atoms attached to ring C atoms and C(6). In the final cycles one scale factor, the atomic coordinates and anisotropic thermal parameters for the heavy atoms (235 parameters in all) were varied. For H atoms the isotropic thermal parameters are those of the bonded atoms. The H atoms were included in structure factor calculations only. The final R ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0·046 for D-*xylo*- and 0·064 for D-*ribo*-aldopyranose.

Scattering factors given by Cromer & Mann (1968) and (for H) by Stewart, Davidson & Simpson (1965) were used.

The calculations were carried out on the Univac 1110 computer at the University Computing Center in Zagreb with the XRAY-72/73 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1973).

Positional and isotropic thermal parameters are listed in Tables 2, 3 for the D-*xylo* and Tables 4, 5 for the D-*ribo* isomer.*

Description and discussion of the structures

The structural formulae and bond lengths for (IV) and (V) are given in Figs. 1 and 2. The $^4H_5$ conformation for both isomers and substituent positions are shown in Fig. 3. Molecular packing is illustrated in Figs. 4 and 5.

Bond angles are listed in Table 6 and displacements of the atoms from the least-squares plane through the sugar rings in Table 7. Torsion angles are given in Table 8.

In the preparation of these unsaturated amino sugars, D compounds were used as the starting materials (Pravdić, Židovec & Fletcher, 1970, 1973). There is no reason to expect conversion from D to L enantiomers. Therefore the D enantiomers were selected and the configuration and conformation defined in accordance with torsion angles for compounds (IV) and (V) (Table 8). The Bijvoet pairs were not measured.

The sugar rings in (IV) and (V) exhibit a half-chair $^4H_5$ conformation (Fig. 3). The best least-squares plane is defined by O(0), C(1), C(2) and C(3); C(4) and C(5) are displaced from this plane (Table 7). In the D-*xylo* compound C(4) is 0·558 above and C(5) 0·164 Å below the plane. This distorted $^4H_5$ conformation can be also described as a transition state to the sofa conformation. The D-*ribo* isomer appears in a very symmetrical $^4H_5$ conformation with C(4) displaced by 0·413 and C(5) −0·407 Å. In some unsaturated (1,2 and 2,3) amino sugars, with substituents attached to C(4) in axial or quasi-axial [and to C(5) in equatorial] positions, distorted half-chair conformations were observed (Rogić, 1975; Kojić-Prodić, Rogić & Ružić-Toroš, 1976). Thus, the $^0H_5$ distorted half-chair conformation [with O(0), displaced by 0·427 and C(5) by 0·287 Å from the best least-squares plane] also occurred in 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranose (Kojić-Prodić, Rogić & Ružić-Toroš, 1976).† However, in

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32807 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† In the cited paper the orientation of the C(1) substituent was denoted as quasi-equatorial, instead of quasi-axial.

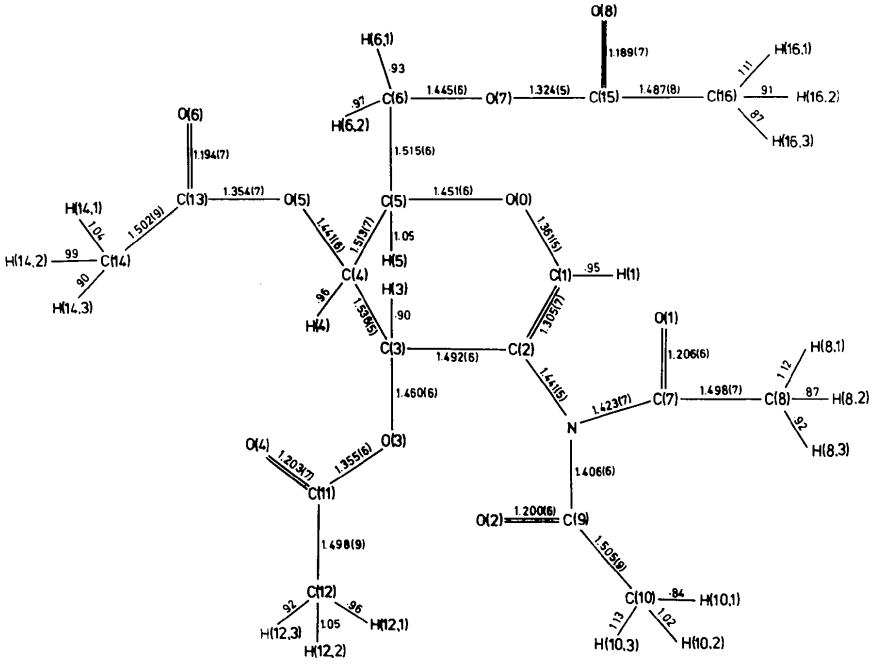


Fig. 1. The structural formula and intramolecular distances for the D-*xylo* compound.

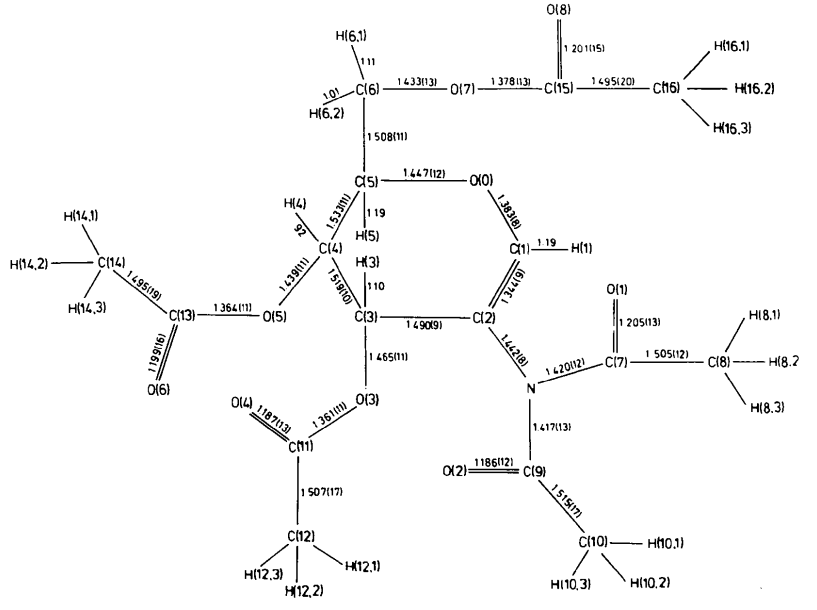


Fig. 2. The structural formula and intramolecular distances for the D-*ribo* compound.

1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranose (Rogić, 1975) with a quasi-equatorial substituent at C(4), a rather symmetrical $^0H_5$ half-chair conformation was found [O(0) is 0·345 above and C(5) 0·364 Å below the least-squares plane]. In these unsaturated amino sugars with substituents at C(4) and C(5) in quasi-equatorial or equatorial position the steric hindrances can be avoided by larger departure of C(5) from the ring plane and thus the more symmetrical half-chair conformation is obtained.

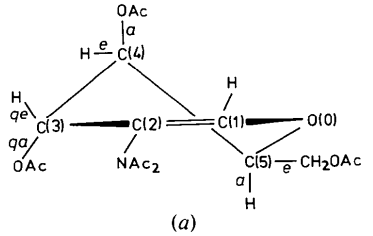
Sundaralingam (1968) has defined the conformation about C(5)–C(6) in pyranosides by the angle φ_{OO} = O(5)–C(5)–C(6)–O(6). In the present structures this angle is described by the sequence O(0)–C(5)–C(6)–O(7); the values of 175·1 (4) for D-*xylo*- and

156·5 (5)° for D-*ribo*-aldopyranose are not in the range common for pyranoside derivatives (+60 ± 30° or −60 ± 30°).

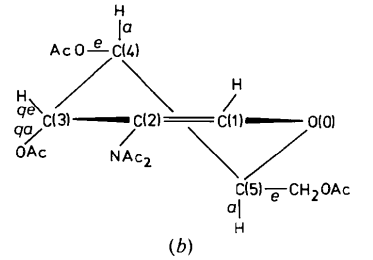
In the D-*xylo* compound substituents are attached to C(3) in quasi-axial, C(4) in axial and C(5) in equatorial positions (Fig. 3) (Stoddart, 1971). The D-*ribo* isomer has the substituents disposed at C(3) in quasi-axial, at C(4) and C(5) in equatorial positions (Fig. 3).

The conformations for both compounds are in full accord with their NMR spectra (Pravdić, Židovec & Fletcher, 1973): the small coupling constant, $J_{4,5} \sim 1$ Hz, for the D-*xylo* isomer (IV) corresponds to equatorial and axial orientations of H(4) and H(5), respectively, whereas the large $J_{4,5} \sim 10$ Hz for the D-*ribo* isomer (V) is indicative of a *trans*-diaxial relationship of the protons.

The mean values of the C–C length in the rings are 1·525 (6) and 1·526 (10) Å for the D-*xylo* and D-*ribo* isomers, respectively. The C(2)–C(3) lengths are shortened to 1·492 (6) (IV) and 1·490 (9) Å (V) because of the presence of the C(1)=C(2) double bond. In the acetyl groups the mean C–C lengths are 1·498 (8) (IV) and 1·503 (17) Å (V). There are several categories of C–O bonds: the mean values of (C–)C–O bonds in *O*-acetyl groups are 1·448 (6) (IV) and 1·446 (12) Å (V); the (O=)C–O bonds have mean values of 1·344 (6) (IV) and 1·368 (12) Å (V); endocyclic C(1)–O(0) [1·361 (5) (IV), 1·383 (8) Å (V)] and C(5)–O(0) [1·451 (6) (IV), 1·447 (12) Å (V)] are asymmetric; the mean values of bonds are 1·198 (6) (IV) and 1·196 (14) Å (V).



(*a*)



(*b*)

Fig. 3. Schematic drawing of $^4H_5$ half-chair conformation illustrating the displacement of C(4) (above) and C(5) (below) the plane defined by O(0), C(1), C(2) and C(3), and orientation of substituents, in (*a*) D-*xylo* isomer (IV), (*b*) D-*ribo* isomer (V).

The mean values of angles at the endocyclic C atoms are 109·9 (4) (IV) and 108·3 (6)° (V). Those of the ring O atoms are 116·1 (3) (IV) and 115·4 (6)° (V), *i.e.* greater than the hypothetical value for the pyranose ring, 113·3° (Kim & Jeffrey, 1967). In 1,4,6-tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranose (I) (Kojić-Prodić, Rogić & Ružić-Toroš, 1976) the angle at the ring O atom is 112·5 (2)°. The enlargement in the present structures could be due to the influence of the C(1)=C(2) double bond next to the ring O atom. The C valence angles exterior to the

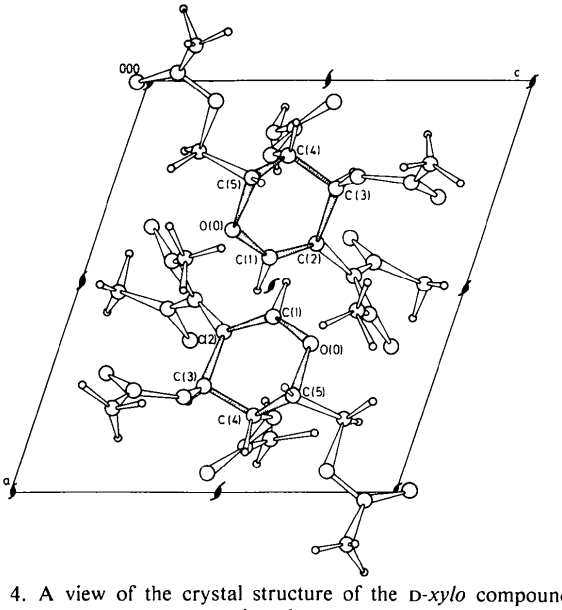


Fig. 4. A view of the crystal structure of the D-*xylo* compound along **b**.

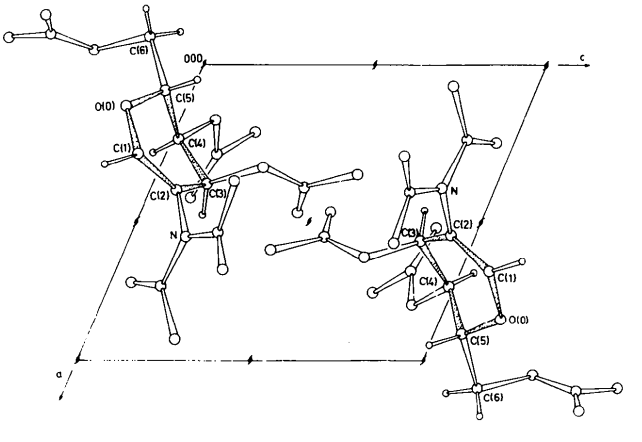


Fig. 5. A view of the crystal structure of the D-*ribo* compound along **b**.

Table 6. *Bond angles* (°)

	D-*xylo*	D-*ribo*
Pyranose ring		
O(0)–C(1)–C(2)	125·8 (4)	121·7 (5)
C(1)–C(2)–C(3)	122·1 (3)	124·3 (5)
C(2)–C(3)–C(4)	108·7 (4)	108·3 (6)
C(3)–C(4)–C(5)	109·4 (3)	108·8 (6)
C(4)–C(5)–O(0)	111·6 (3)	107·9 (7)
C(5)–O(0)–C(1)	116·1 (3)	115·4 (6)
O(0)–C(1)–H(1)	111	112
C(2)–C(1)–H(1)	123	125
C(1)–C(2)–N	119·8 (4)	117·0 (5)
N–C(2)–C(3)	117·9 (4)	118·7 (6)
C(2)–C(3)–H(3)	115	102
H(3)–C(3)–O(3)	108	118
C(2)–C(3)–O(3)	112·2 (3)	107·0 (6)
H(3)–C(3)–C(4)	108	110
O(3)–C(3)–C(4)	104·1 (3)	110·3 (7)
H(4)–C(4)–O(5)	108	100
H(4)–C(4)–C(3)	111	120
C(3)–C(4)–O(5)	109·2 (4)	111·4 (6)
C(5)–C(4)–H(4)	111	109
O(5)–C(4)–C(5)	107·7 (4)	106·9 (7)
C(4)–C(5)–H(5)	110	106
C(4)–C(5)–C(6)	113·8 (4)	116·6 (7)
C(6)–C(5)–O(0)	104·5 (4)	107·8 (7)
C(6)–C(5)–H(5)	109	100
H(5)–C(5)–O(0)	107	118
O(3)-acetyl group		
C(3)–O(3)–C(11)	116·8 (4)	116·8 (7)
O(3)–C(11)–O(4)	122·7 (5)	123·7 (9)
O(3)–C(11)–C(12)	110·4 (4)	110·9 (9)
O(4)–C(11)–C(12)	126·9 (5)	125·3 (9)
C(11)–C(12)–H(12,1)	114	
C(11)–C(12)–H(12,2)	111	
C(11)–C(12)–H(12,3)	105	
H(12,1)–C(12)–H(12,2)	111	
H(12,1)–C(12)–H(12,3)	105	
H(12,2)–C(12)–H(12,3)	109	
N-acetyl groups		
C(2)–N–C(7)	114·7 (3)	114·7 (7)
N–C(7)–O(1)	118·2 (4)	118·4 (8)
N–C(7)–C(8)	118·9 (4)	119·7 (9)
O(1)–C(7)–C(8)	122·7 (5)	121·9 (9)
C(7)–C(8)–H(8,1)	110	
C(7)–C(8)–H(8,2)	112	
C(7)–C(8)–H(8,3)	108	
H(8,1)–C(8)–H(8,2)	107	
H(8,1)–C(8)–H(8,3)	113	
H(8,2)–C(8)–H(8,3)	108	
C(7)–N–C(9)	123·5 (4)	124·4 (7)
C(2)–N–C(9)	121·7 (3)	120·9 (7)
N–C(9)–C(10)	116·8 (4)	116·6 (8)
N–C(9)–O(2)	122·0 (5)	123 (1)
O(2)–C(9)–C(10)	121·2 (5)	120 (1)
C(9)–C(10)–H(10,1)	114	
C(9)–C(10)–H(10,2)	111	
C(9)–C(10)–H(10,3)	111	
H(10,1)–C(10)–H(10,2)	112	
H(10,1)–C(10)–H(10,3)	105	
H(10,2)–C(10)–H(10,3)	103	

Table 6 (*cont.*)

O(5)-acetyl group		
C(4)–O(5)–C(13)	116·3 (4)	116·2 (8)
O(5)–C(13)–O(6)	123·3 (5)	122·4 (9)
O(5)–C(13)–C(14)	110·7 (5)	111 (1)
O(6)–C(13)–C(14)	125·9 (6)	126·8 (9)
C(13)–C(14)–H(14,1)	103	
C(13)–C(14)–H(14,2)	100	
C(13)–C(14)–H(14,3)	116	
H(14,1)–C(14)–H(14,2)	115	
H(14,1)–C(14)–H(14,3)	108	
H(14,2)–C(14)–H(14,3)	113	
C(6) -O(7)-acetyl group		
C(5)–C(6)–O(7)	104·5 (4)	111·7 (8)
C(5)–C(6)–H(6,1)	113	106
C(5)–C(6)–H(6,2)	114	98
H(6,1)–C(6)–H(6,2)	102	103
H(6,1)–C(6)–O(7)	113	120
H(6,2)–C(6)–O(7)	110	115
C(6)–O(7)–C(15)	117·4 (4)	117·6 (8)
O(7)–C(15)–O(8)	121·6 (5)	122 (1)
O(7)–C(15)–C(16)	112·0 (5)	112 (1)
O(8)–C(15)–C(16)	126·3 (5)	126 (1)
C(15)–C(16)–H(16,1)	102	
C(15)–C(16)–H(16,2)	115	
C(15)–C(16)–H(16,3)	103	
H(16,1)–C(16)–H(16,2)	112	
H(16,1)–C(16)–H(16,3)	105	
H(16,2)–C(16)–H(16,3)	118	

Table 7. *Displacements of atoms from the least-squares plane through the sugar rings* (Å)

Atoms included in the calculation of the plane are denoted by an asterisk.

D-*xylo* isomer (IV)		D-*ribo* isomer (V)	
C(1)*	0·021	C(1)*	0·015
C(2)*	−0·019	C(2)*	−0·015
C(3)*	0·008	C(3)*	0·007
C(4)	0·558	C(4)	0·413
C(5)	−0·164	C(5)	0·407
O(0)*	−0·010	O(0)*	−0·007

pyranose ring are in the range 104·1 (3) to 113·8 (4)° in (IV) and 106·9 (7) to 116·6 (7)° in (V).

All hydroxyl groups are acetylated and O–H···O hydrogen bonds are not possible. The intermolecular distances give no evidence of C–H···O hydrogen bonds. In the crystal molecules are connected by van der Waals forces only.

Table 8. *Torsion angles* (°)

	D-*xylo*	D-*ribo*
In the pyranose ring		
O(0)–C(1)–C(2)–C(3)	−5·1 (3)	−3·8 (6)
C(1)–C(2)–C(3)–C(4)	−18·9 (4)	−13·9 (6)
C(2)–C(3)–C(4)–C(5)	48·4 (5)	47·3 (4)
C(3)–C(4)–C(5)–O(0)	−58·4 (5)	−66·6 (5)
C(4)–C(5)–O(0)–C(1)	35·5 (5)	49·4 (7)
C(5)–O(0)–C(1)–C(2)	−3·2 (4)	−15·2 (6)
On the pyranose ring		
O(0)–C(1)–C(2)–N	179·3 (3)	175·4 (4)
C(1)–C(2)–C(3)–H(3)	−139	−130
C(2)–C(3)–C(4)–H(4)	171	−79
C(2)–C(3)–C(4)–O(5)	−69·1 (4)	164·8 (4)
C(3)–C(4)–C(5)–H(5)	61	61
C(3)–C(4)–C(5)–C(6)	−176·4 (4)	172·0 (4)
C(5)–O(0)–C(1)–H(1)	173	175
C(1)–C(2)–C(3)–O(3)	95·8 (3)	105·0 (4)
H(5)–C(5)–O(0)–C(1)	−86	−71
C(6)–C(5)–O(0)–C(1)	159·0 (3)	176·2 (5)
H(4)–C(4)–C(5)–O(0)	179	66
O(5)–C(4)–C(5)–O(0)	60·2 (4)	173·0 (4)
H(1)–C(1)–C(2)–N	4	−16
N–C(2)–C(3)–H(3)	36	51
N–C(2)–C(3)–O(3)	−88·6 (3)	−74·2 (4)
H(3)–C(3)–C(4)–H(4)	−64	31
H(3)–C(3)–C(4)–O(5)	56	−84
O(3)–C(3)–C(4)–H(4)	51	164
O(3)–C(3)–C(4)–O(5)	171·0 (3)	48·0 (7)
H(4)–C(4)–C(5)–H(5)	−62	−166
H(4)–C(4)–C(5)–C(6)	61	−55
O(5)–C(4)–C(5)–H(5)	180	−59
O(5)–C(4)–C(5)–C(6)	−57·9 (5)	51·6 (5)
Acetyl groups		
C(2)–N–C(7)–O(1)	−15·3 (7)	−6·2 (8)
C(2)–N–C(7)–C(8)	160·8 (4)	172·1 (6)
C(2)–N–C(9)–O(2)	167·1 (5)	178·4 (5)
C(2)–N–C(9)–C(10)	−13·0 (7)	0·1 (8)
C(8)–C(7)–N–C(9)	−17·1 (7)	−9·4 (9)
O(1)–C(7)–N–C(9)	166·8 (5)	172·2 (6)
C(7)–N–C(9)–O(2)	−15·1 (8)	0·0 (9)
C(7)–N–C(9)–C(10)	−164·8 (5)	−178·2 (6)
C(3)–O(3)–C(11)–O(4)	−8·6 (7)	4·3 (9)
C(3)–O(3)–C(11)–C(12)	172·8 (4)	−174·5 (5)
C(4)–O(5)–C(13)–O(6)	−1·6 (6)	3·1 (7)
C(4)–O(5)–C(13)–C(14)	177·2 (4)	−177·7 (4)
C(5)–C(6)–O(7)–C(15)	−179·3 (5)	130·7 (9)
C(6)–O(7)–C(15)–O(8)	−0·8 (9)	32·0 (8)
C(6)–O(7)–C(15)–C(16)	−179·8 (5)	−157·6 (7)
H(3)–C(3)–O(3)–C(11)	−37	32
H(4)–C(4)–O(5)–C(13)	45	−48
H(5)–C(5)–C(6)–O(7)	61	32
H(5)–C(5)–C(6)–H(6,1)	−63	−59
H(5)–C(5)–C(6)–H(6,2)	179	47
Others		
C(1)–C(2)–N–C(7)	113·4 (4)	104·1 (5)
C(1)–C(2)–N–C(9)	−68·6 (4)	−74·4 (6)
C(2)–C(3)–O(3)–C(11)	−91·1 (4)	146·7 (5)
C(3)–C(4)–O(5)–C(13)	−76·4 (4)	79·8 (6)
C(3)–C(2)–N–C(7)	−62·3 (5)	−76·6 (5)
C(3)–C(2)–N–C(9)	115·6 (4)	104·9 (6)
C(4)–C(3)–O(3)–C(11)	−151·4 (4)	−95·6 (6)
C(4)–C(5)–C(6)–O(7)	−62·8 (5)	−81·9 (3)
C(4)–C(5)–C(6)–H(6,1)	173	−173
C(4)–C(5)–C(6)–H(6,2)	58	−67
O(0)–C(5)–C(6)–O(7)	175·1 (4)	156·6 (5)
O(0)–C(5)–C(6)–H(6,1)	51	65
O(0)–C(5)–C(6)–H(6,2)	−64	171
H(6,1)–C(6)–O(7)–C(15)	−56	−124
H(6,2)–C(6)–O(7)–C(15)	58	−18
O(0)–C(5)–C(6)–H(6,1)	51	65
O(0)–C(5)–C(6)–H(6,2)	−64	171

The authors thank MSc Milenko Bruvo for collecting the intensities at the Department of General and Inorganic Chemistry, Faculty of Science, University of Zagreb.

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