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The Crystal and Molecular Structure of α-Xylose

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The crystals of α-xylose belong to the orthorhombic space group $P2_12_12_1$, with unit cell dimensions $a = 9.247(12)$ Å, $b = 12.666(10)$ Å, and $c = 5.635(9)$ Å. There are four molecules per unit cell.

The structure has been refined by least squares method. The refinement comprises 796 *hk*0 – *hk*5 reflections, including 45 unobserved.

α-Xylose occurs in the conversion form 1*a*2*e*3*e*4*e*. The carbon-carbon bond lengths are C(1) – C(2) = 1.531(6) Å, C(2) – C(3) = 1.529(6) Å, C(3) – C(4) = 1.515(6) Å, and C(4) – C(5) = 1.503(7) Å. The lengths of the carbon-oxygen bonds in the pyranose ring, C(1) – O(5) and C(5) – O(5), are 1.428(4) and 1.449(6) Å, respectively, and the other C – O bond lengths in the molecule are C(1) – O(1) = 1.393(6) Å, C(2) – O(2) = 1.415(5) Å, C(3) – O(3) = 1.418(6) Å, and C(4) – O(4) = 1.411(5) Å. The C(1) – O(5) – C(5) angle is 112.4(3)°.

In the crystal, there is a complete set of hydrogen bonds: $O_1 \cdots O_2' = 2.743(5)$ Å, $O_2 \cdots O_4' = 2.749(5)$ Å, $O_3 \cdots O_5' = 2.808(5)$ Å, and $O_4 \cdots O_3' = 2.687(5)$ Å.

A Fourier *c*-projection of the molecular structure of α-xylose was reported in 1958 by Woolfson.[1] The structure had been solved by means of direct methods.

At about the same time, and independently, the present author obtained the structure solution by systematic application of Sayre's equation.[2] Earlier, the structure of β-arabinose had been solved in this way.[3,4]

The author has now, in understanding with Professor Woolfson, carried out a refinement of the molecular structure of α-xylose.

EXPERIMENTAL

α-Xylose, crystallized from a water-ethanol (1 : 2) mixture as orthorhombic needles, elongated along the *c*-axis. The crystals belong to the space group $P2_12_12_1$ with $Z = 4$.

The unit cell dimensions were determined from high-order reflections on 0*kl* and *hk*0 Weissenberg photographs, where sodium chloride powder lines had been superimposed for reference ($a_{\text{NaCl}} = 5.6394$ Å). A least squares procedure on 25 measured 2θ-values gave $a = 9.247(12)$ Å, $b = 12.666(10)$ Å, and $c = 5.635(9)$ Å.

The intensities of the *hk*0 – *hk*5 and 0*kl* reflections were estimated visually from Weissenberg photographs, taken with Ni-filtered Cu*K*α radiation ($\mu = 12.1$ cm^{-1}). 0*kl* reflections from the zero layer about *a* were used for scaling only.

Lp corrections and absorption corrections were applied, the latter according to a procedure of Coppens *et al.*[5] The dimensions of the intensity crystal was 0.2 × 0.2 × 0.4 mm in each of the three axial directions. A grid of 8 × 8 × 12 points was used in correcting for absorption.

The scattering factors used for carbon, oxygen, and hydrogen in the structure factor calculations were those given in the *International Tables.*[6]

The structure was refined by a full-matrix least squares procedure which minimizes the function

$$r = \sum W(|F_o| - K|F_c|)^2$$

with $W = [(Ka_1)^2 + (a_2F_o)^2/4W_o]^{-1}$. W_o, in the weighting scheme, is an individual weight which is estimated from the assumed reliability of the intensity measurement. The constants a_1 and a_2 were in the present case set equal to 1.0. Unobserved reflections with $K|F_c|$ greater than $F_o^{\text{threshold}}$ were included in the refinement with $F_o = F_o^{\text{threshold}}$. Anisotropic temperature factors were applied to sulphur and carbon, and a constant temperature factor $\exp(-2\sin^2\theta/\lambda^2)$ was applied to the hydrogen atoms.

A final refinement cycle was carried out by Shiono's version of the full-matrix least-squares IBM 7090 program by Busing *et al.*[7,8] Hughes' weighting scheme with $F_{\text{min}} = 1.0$ was used.[7] All parameter shifts were negligible in this refinement cycle. The final R factor is 7.5 % when unobserved reflections are included, and 7.2 % when they are omitted.

Final atomic coordinates from the least squares refinement are listed in Table 1, and the temperature parameters in Table 2. The final list of structure factors is given in, Table 6.

Table 1. Atomic coordinates in fractions of corresponding cell edges. Standard deviations, referring to last digits, are given in parentheses.

	x	y	z
C(1)	0.56916(48)	0.48652(33)	0.43950(92)
C(2)	0.64051(44)	0.39827(31)	0.29548(84)
C(3)	0.54617(46)	0.29911(30)	0.29027(78)
C(4)	0.39646(50)	0.32798(31)	0.20255(83)
C(5)	0.33537(51)	0.41665(36)	0.34888(102)
O(1)	0.56098(46)	0.45744(29)	0.67751(68)
O(2)	0.78339(35)	0.38082(26)	0.37632(71)
O(3)	0.61647(44)	0.22720(26)	0.13574(88)
O(4)	0.30547(33)	0.23878(25)	0.21814(67)
O(5)	0.42928(34)	0.50823(23)	0.34366(79)
H(1)	0.607(7)	0.560(5)	0.405(11)
H(2)	0.637(6)	0.429(5)	0.127(13)
H(3)	0.536(7)	0.269(5)	0.446(12)
H(4)	0.391(7)	0.346(5)	0.060(14)
H(5)	0.317(7)	0.406(5)	0.509(13)
H(6)	0.242(7)	0.450(5)	0.261(12)
H(7)	0.577(7)	0.531(5)	0.776(12)
H(8)	0.758(7)	0.369(5)	0.532(13)
H(9)	0.612(8)	0.187(6)	0.145(14)
H(10)	0.240(6)	0.231(5)	0.085(11)

DISCUSSION OF RESULTS

It is found (*cf.* Fig. 1a) that α-xylose in the crystalline state has the conversion form 1*a*2*e*3*e*4*e*, which from Reeves' stability scheme[9] possesses one instability unit against 4.5 for the alternative form 1*e*2*a*3*a*4*a*.

Table 2. Temperature parameters β_{ij} for carbon and oxygen. The expression used is $\exp-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})$. The standard deviations in parentheses refer to the last digits of respective values. All values are multiplied by 10^4. For the hydrogen atoms, a temperature factor $\exp[-2(\sin^2\theta/\lambda^2)]$ was used.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	97(5)	38(2)	193(17)	−6(3)	−19(7)	3(4)
C(2)	77(4)	43(2)	175(16)	−4(3)	4(6)	12(4)
C(3)	83(4)	35(2)	169(15)	−3(2)	17(6)	5(4)
C(4)	98(5)	38(2)	151(15)	−15(3)	−17(7)	13(5)
C(5)	94(5)	48(3)	234(18)	1(3)	−19(8)	−15(5)
O(1)	148(5)	57(2)	204(14)	−28(3)	−19(6)	−3(4)
O(2)	76(3)	57(2)	247(13)	−6(2)	−8(5)	40(4)
O(3)	120(4)	35(2)	403(16)	−2(2)	95(7)	−20(5)
O(4)	95(4)	46(2)	259(13)	−26(2)	−37(6)	21(4)
O(5)	102(4)	32(2)	356(15)	9(2)	−44(6)	−5(4)

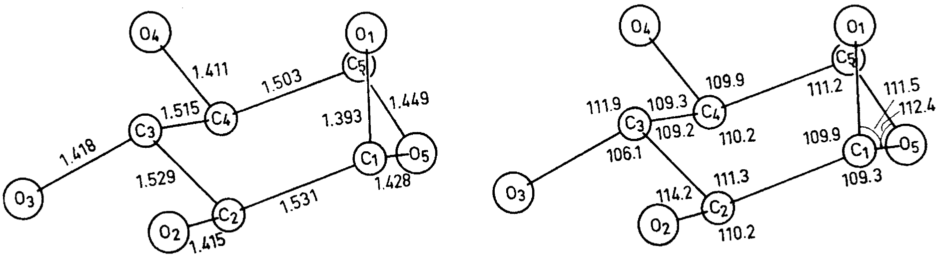
Table 3. Bond lengths D(ij) in α-xylose. The standard deviations given in parentheses refer to the last digits of the respective values.

i	j	D(ij)	i	j	D(ij)
C(1)	C(2)	1.531(6) Å	C(1)	H(1)	1.01(6) Å
C(2)	C(3)	1.529(6)	C(2)	H(2)	1.03(7)
C(3)	C(4)	1.515(6)	C(3)	H(3)	0.96(7)
C(4)	C(5)	1.503(7)	C(4)	H(4)	0.84(8)
C(1)	O(1)	1.393(6)	C(5)	H(5)	0.93(7)
C(2)	O(2)	1.415(5)	C(5)	H(6)	1.08(7)
C(3)	O(3)	1.418(6)	O(1)	H(7)	1.09(6)
C(4)	O(4)	1.411(5)	O(2)	H(8)	0.92(5)
C(5)	O(5)	1.449(6)	O(3)	H(9)	0.81(7)
C(1)	O(5)	1.428(4)	O(4)	H(10)	0.97(6)

Table 4. Bond angles ∠(ijk) in α-xylose. The standard deviations given in parentheses refer to the last digits of the respective values.

i	j	k	∠(ijk)	i	j	k	∠(ijk)
C(1)	C(2)	C(3)	111.3(3)	O(5)	C(1)	H(1)	93(4)
C(2)	C(3)	C(4)	109.2(3)	O(1)	C(1)	H(1)	117(4)
C(3)	C(4)	C(5)	110.2(4)	C(2)	C(1)	H(1)	115(4)
C(4)	C(5)	O(5)	111.2(4)	C(1)	C(2)	H(2)	102(4)
C(5)	O(5)	C(1)	112.4(3)	C(3)	C(2)	H(2)	106(3)
O(5)	C(1)	C(2)	109.3(4)	O(2)	C(2)	H(2)	113(3)
O(5)	C(1)	O(1)	111.5(3)	C(2)	C(3)	H(3)	111(4)
C(2)	C(1)	O(1)	109.9(3)	C(4)	C(3)	H(3)	108(4)
C(1)	C(2)	O(2)	110.2(3)	O(3)	C(3)	H(3)	111(4)
C(3)	C(2)	O(2)	114.2(3)	C(3)	C(4)	H(4)	116(4)
C(2)	C(3)	O(3)	106.1(3)	C(5)	C(4)	H(4)	107(4)
C(4)	C(3)	O(3)	111.9(4)	O(4)	C(4)	H(4)	104(4)
C(3)	C(4)	O(4)	109.3(3)	C(4)	C(5)	H(5)	120(4)
C(5)	C(4)	O(4)	109.9(4)	O(5)	C(5)	H(5)	104(4)
C(1)	O(1)	H(7)	105(3)	C(4)	C(5)	H(6)	110(4)
C(2)	O(2)	H(8)	95(4)	O(5)	C(5)	H(6)	99(3)
C(3)	O(3)	H(9)	123(9)	H(5)	C(5)	H(6)	111(5)
C(4)	O(4)	H(10)	114(4)				

Bond lengths and angles for the α-xylose molecule, as derived from the coordinates in Table 1, are listed in Tables 3 and 4, and are, apart from those involving hydrogen, shown in Figs. 1a and 1b. The carbon-carbon bond lengths are in the range 1.503 to 1.531 ± 0.007 Å, and the cyclic C – O bonds, C(1) – O(5) and C(5) – O(5), are 1.428(4) and 1.449(6) Å, respectively. The anomeric C – O bond, C(1) – O(1), is 1.393(6) Å, and the C – O(hydroxyl) bonds vary from 1.411 to 1.418 ± 0.006 Å.



(a) (b)

Fig. 1. (a) Bond lengths (Å) in the α-xylose molecule. (b) Bond angles (°).

The results from the present study may be compared with those from the studies of β-arabinose [4,10] and β-lyxose.[11] So far, the structures of these three aldopentoses only have been investigated. A comparison of bond lengths in β-arabinose, α-xylose, and β-lyxose is given in Table 5. Two sets of bond lengths for β-arabinose are given. They are from the present author's investigation of β-arabinose by two-dimensional methods,[4] and from Kim and Jeffrey's

Table 5. Comparison of bond lengths in α-xylose with bond lengths in β-arabinose, β-lyxose, and α-glucose.

		X-Ray diffraction				Neutron diffraction
		β-Arabinose		α-Xylose	β-Lyxose	α-Glucose
			DL			
Anomeric C – O bond	C(1) – O(1)	1.382(12)	1.392(4)	1.393(6)	1.364(6)	1.389(6)
C – O(hydroxyl) bonds	C(2) – O(2)	1.454(8)	1.417(4)	1.415(5)	1.399(6)	1.415(3)
	C(3) – O(3)	1.426(9)	1.432(4)	1.418(6)	1.430(5)	1.415(3)
	C(4) – O(4)	1.431(12)	1.425(4)	1.411(5)	1.405(6)	1.425(3)
Cyclic C – O bonds	C(1) – O(5)	1.421(8)	1.434(4)	1.428(4)	1.435(6)	1.426(3)
	C(5) – O(5)	1.440(8)	1.447(4)	1.449(6)	1.422(6)	1.427(3)
C – C bonds	C(1) – C(2)	1.529(9)	1.532(4)	1.531(6)	1.538(7)	1.534(3)
	C(2) – C(3)	1.523(9)	1.528(4)	1.529(6)	1.528(7)	1.525(3)
	C(3) – C(4)	1.554(9)	1.533(4)	1.515(6)	1.509(7)	1.519(3)
	C(4) – C(5)	1.537(10)	1.515(4)	1.503(7)	1.525(6)	1.528(3)

Table 6. Observed and calculated structure factors for α-xylose. The values given are ten times the absolute values. The columns are: Index, $|F_{obs}|$, $|F_{calc}|$, A_{calc}, B_{calc}. Unobserved reflections are marked with asterisks.

L= 0 H= 0				
2	102	92	92	0
4	458	484	484	0
6	119	124	124-	0
8	212	237	237	0
10	104	118	118	0
12	66	58	58	0
14	23	17	17-	0
16	7*	7	7	0
L= 0 H= 1				
1	209	214	0	214
2	449	472	0	472
3	87	77	0	77-
4	130	148	0	148
5	183	222	0	222-
6	96	109	0	109
7	40	43	0	43
8	105	101	0	101
9	96	104	0	104
10	111	126	0	126-
11	73	81	0	81-
12	111	104	0	104
13	97	98	0	98-
14	43	42	0	42-
15	15*	5	0	5-
16	13	13	0	13
L= 0 H= 2				
0	87	88	88	0
1	48	58	58-	0
2	347	367	367	0
3	53	45	45	0
4	459	443	443	0
5	278	299	299-	0
6	393	402	402	0
7	77	90	90-	0
8	131	139	139-	0
9	62	60	60-	0
10	75	75	75	0
11	157	161	161-	0
12	24	16	16-	0
13	12*	16	16	0
14	42	40	40	0
15	47	47	47-	0
L= 0 H= 3				
1	19	14	0	14
2	28	25	0	25-
3	283	318	0	318
4	227	247	0	247-
5	80	72	0	72-
6	185	194	0	194
7	129	123	0	123-
8	22	26	0	26-
9	127	145	0	145-
10	177	183	0	183
11	13*	7	0	7-
12	69	69	0	69-
13	89	95	0	95-
14	35	31	0	31-
15	31	27	0	27
L= 0 H= 4				
0	290	302	302-	0
1	477	454	454-	0
2	30	25	25	0
3	51	51	51-	0
4	60	62	62-	0
5	299	322	322-	0
6	38	36	36	0
7	22	17	17	0
8	46	44	44	0
9	130	120	120-	0
10	31	31	31-	0
11	90	84	84-	0
12	76	79	79-	0
13	19	21	21-	0
14	12	10	10-	0
15	33	37	37-	0
L= 0 H= 5				
1	159	165	0	165
2	178	180	0	180-
3	78	80	0	80-
4	24*	5	0	5
5	61	56	0	56
6	90	88	0	88
7	91	98	0	98-
8	72	64	0	64-
9	25	27	0	27-
10	16*	1	0	1-
11	54	51	0	51-
12	30	27	0	27-
13	29	26	0	26-
14	10	13	0	13
L= 0 H= 6				
0	210	204	204-	0
1	152	159	159	0
2	124	137	137-	0
3	43	44	44-	0
4	144	149	149-	0
5	29	29	29	0
6	178	204	204-	0
7	274	291	291-	0
8	52	38	38-	0
9	41	41	41	0
10	13*	12	12-	0
11	31	28	28-	0
12	10*	2	2	0
13	9*	0	0	0
14	5*	7	7-	0
L= 0 H= 7				
1	35	31	0	31
2	120	112	0	112
3	99	101	0	101-
4	60	60	0	60
5	189	193	0	193
6	142	157	0	157-
7	43	43	0	43-
8	76	64	0	64-
9	38	30	0	30
10	11	11	0	11
11	54	47	0	47-
12	24	26	0	26
L= 0 H= 8				
0	127	134	134-	0
1	107	108	108-	0
2	90	97	97-	0
3	13*	13	13-	0
4	128	137	137-	0
5	78	69	69	0
6	50	49	49-	0
7	25	19	19	0
8	38	37	37-	0
9	11*	9	9-	0
10	17	18	18-	0
11	33	33	33-	0
L= 0 H= 9				
1	30	24	0	24
2	94	92	0	92-
3	13	12	0	12-
4	44	42	0	42-
5	12*	2	0	2-
6	23	18	0	18-
7	16	15	0	15
8	59	58	0	58
9	9*	8	0	8
10	40	42	0	42-
L= 0 H= 10				
0	12	13	13-	0
1	23	27	27-	0
2	70	77	77-	0
3	40	44	44	0
4	11*	5	5	0
5	28	27	27-	0
6	9*	6	6-	0
7	38	36	36	0
8	25	28	28	0
L= 0 H= 11				
1	9*	8	0	8
2	9*	1	0	1-
3	8*	9	0	9
4	11	11	0	11
5	30	35	0	35-
L= 1 H= 0				
2	541	535	535	0
3	533	552	0	552-
4	63	59	59-	0
5	58	49	0	49
6	347	354	354-	0
7	26	19	0	19
8	79	73	73-	0
9	20	16	0	16
10	174	181	181-	0
11	92	86	0	86-
12	141	142	142	0
13	15	9	0	9-
14	57	53	53-	0
15	9*	6	0	6
16	25	32	32	0
L= 1 H= 1				
1	494	473	471-	44-
2	403	403	236	327
3	275	322	278-	163
4	185	212	68-	201-
5	296	317	250-	196-
6	65	63	29-	56-
7	92	81	23	78-
8	78	84	23	81-
9	119	129	128-	16-
10	189	202	107	171-
11	155	160	8-	159
12	107	106	31	101-
13	58	58	49-	32-
14	41	36	0	36-
15	21	19	3-	19
L= 1 H= 2				
0	83	81	0	81
1	335	346	338-	75
2	201	211	189-	94-
3	183	200	68-	188
4	353	355	355-	0
5	199	219	165-	144-
6	135	148	102	107-
7	129	128	52-	117-
8	111	106	80-	69
9	70	61	57	23-
10	56	49	39-	30
11	18	13	6	11
12	31	28	25-	13
13	56	51	51-	0
14	42	35	1	35
15	12	11	8	8-
L= 1 H= 3				
0	405	417	0	417
1	184	172	53-	163
2	117	119	46	109-
3	296	327	36-	325-
4	98	100	34-	94
5	197	206	50-	199
6	347	350	250	245-
7	171	167	122-	115-
8	55	47	42	22
9	12*	15	13	7
10	86	82	58	58-
11	56	54	1-	54
12	75	73	13	72
13	51	48	41	24
14	72	74	63	38-
15	59	65	24-	60
L= 1 H= 4				
0	238	226	0	226-
1	233	241	160-	180-
2	125	131	58-	118-
3	189	211	201-	64
4	148	140	93-	105
5	166	169	168-	12
6	86	75	75	6
7	47	44	37-	24
8	65	64	57-	30
9	37	34	3	34-
10	107	100	99	14-
11	43	37	34	14-
12	71	65	60-	25
13	47	41	39-	15
14	40	38	36-	14
15	48	58	57	8
L= 1 H= 5				
0	161	157	0	157
1	165	153	147	42
2	143	132	117	61
3	74	64	46	44-
4	134	128	90	91-
5	86	76	42	64-
6	158	160	43	154
7	52	47	38	28
8	58	50	36	34
9	97	101	93	40-
10	79	83	32	76
11	43	36	23-	28
12	47	41	41	5
13	12	7	6	1-
14	14	12	10	7
L= 1 H= 6				
0	26	20	0	20-
1	126	126	123-	30-
2	69	66	37	55
3	138	138	138-	13
4	212	215	144	159-
5	177	173	173	3
6	23	13	1-	13
7	117	111	107-	26
8	32	27	18-	20
9	45	42	7-	42
10	17	21	11-	18
11	44	31	20-	24
12	14	9	9	1-
13	44	50	49	11-
L= 1 H= 7				
0	66	59	0	59-
1	59	54	40	36-
2	83	66	50-	43-
3	133	134	133	10
4	172	177	16	177
5	170	173	127	118-
6	104	101	2-	101
7	112	110	44	101
8	59	53	42	33
9	44	45	4-	44-
10	11*	9	0	9
11	27	23	17	16
12	51	55	21	51
L= 1 H= 8				
0	56	52	0	52-
1	86	77	65	42
2	53	37	32	20
3	99	93	93-	4
4	61	55	55	8
5	42	39	27	29
6	12*	6	3-	5
7	32	23	10	21
8	67	60	36	48-
9	36	36	35	7
10	22	20	7	19-
11	14	15	13	7
L= 1 H= 9				
0	53	42	0	42
1	125	128	90	91
2	43	39	7-	38
3	40	41	11	39-
4	34	30	13-	27-
5	39	36	7-	36
6	14	10	9-	5-
7	48	48	29	39-
8	43	36	28-	23
9	30	27	17	21-
10	55	68	9-	68
L= 1 H= 10				
0	33	32	0	32
1	46	44	31	31
2	19	19	15-	12-
3	50	45	44	11-
4	10*	7	2	7
5	31	25	13-	21
6	18	14	14-	2-
7	8*	6	3-	5
8	61	74	71	19
L= 1 H= 11				
0	9	6	0	6-
1	15	12	12-	3-
2	23	20	19	7-
3	28	28	2-	28
4	10	15	13-	7-
5	15	15	14	4
L= 2 H= 0				
1	473	480	0	480
2	173	189	189	0
3	67	65	0	65-
4	119	133	133-	0
5	74	73	0	73
6	78	88	88	0
7	23	21	0	21-
8	37	41	41	0
9	347	359	0	359
10	12*	6	6	0
11	38	40	0	40
12	15*	9	9-	0
13	83	89	0	89
14	41	41	41	0
15	23	17	0	17
L= 2 H= 1				
0	68	71	71-	0
1	176	199	198	15
2	214	246	115	218-
3	72	70	52-	47
4	215	232	230	26
5	117	146	134	58
6	60	52	26-	45-
7	95	105	71	77
8	90	89	87-	20
9	124	126	116	51-
10	83	78	14-	76
11	61	52	13-	51
12	46	44	36	25-
13	21	18	3-	18
14	70	71	52	48
15	23	23	14-	17
L= 2 H= 2				
0	24	27	27-	0
1	124	122	38-	116-
2	113	106	105-	16
3	227	228	167	154
4	242	264	64	256
5	225	242	12	242
6	156	154	122-	94-
7	55	56	12-	55
8	112	114	112	18
9	63	61	54-	27
10	78	81	52-	62-
11	102	103	83	61
12	68	65	56	33-
13	64	60	43-	42
14	60	60	5-	60-
15	33	39	2-	38
L= 2 H= 3				
0	331	346	346	0
1	183	187	187-	2
2	87	84	72	42
3	194	223	221	33
4	161	170	131	108
5	107	117	30	113
6	132	148	76-	127-
7	108	122	45	114
8	133	135	133	22
9	64	60	56-	22
10	70	61	22-	57-
11	51	48	9-	47
12	72	59	29-	51
13	76	75	36	66
14	27	26	16	21
L= 2 H= 4				
0	106	106	106	0
1	148	149	144	39-
2	182	171	1	171-
3	119	128	100-	80-
4	118	127	104-	74
5	151	154	141	63-
6	13	17	14-	10
7	85	82	6-	82
8	65	66	12-	65
9	78	78	23	75-
10	58	58	30	49-
11	21	15	13-	8
12	44	46	29	36-
13	68	66	32-	58-
14	44	48	15-	45-
L= 2 H= 5				
0	47	47	47-	0
1	65	63	48-	41
2	148	149	133	66
3	97	90	67	60
4	83	76	60	47-
5	92	86	74-	44-
6	76	71	70	14
7	107	113	79-	82
8	29	18	12	13-
9	85	85	40	75
10	40	34	30-	18-
11	65	58	41	42
12	33	28	3	28-
13	27	26	3-	26
14	20	24	19-	15
L= 2 H= 6				
0	32	34	34-	0
1	47	35	27-	22-
2	135	137	26	135
3	84	88	40	78-
4	17	11	11-	4-
5	114	116	51-	104-
6	81	76	68	33-
7	151	160	128	97-
8	73	71	57-	42-
9	93	94	46-	82-
10	63	57	19-	54
11	25	26	24	8-
12	29	27	8-	26-
13	23	28	24-	15-
L= 2 H= 7				
0	12*	12	12-	0
1	78	74	67-	32-
2	108	109	106	25-
3	150	152	132-	76
4	93	95	84-	43-
5	76	73	1-	73-
6	53	47	23	41
7	59	55	41	36
8	38	35	35-	4
9	21	13	12-	4
10	18	17	0	17-
11	20	22	17-	14
12	34	34	23	26-
L= 2 H= 8				
0	39	36	36	0
1	85	91	80	43-
2	44	45	37-	26-
3	43	42	31-	28-
4	71	63	62	6-
5	49	44	3	44-
6	69	65	22-	61
7	55	55	9	55-
8	19	13	3-	13
9	24	22	6	22-
10	34	33	22-	25-
L= 2 H= 9				
0	12*	6	6	0
1	95	97	90	36-
2	43	38	38-	5
3	14	14	14	1-
4	14	10	3	10
5	24	18	18-	0
6	17	15	7-	13
7	46	50	44-	23-
8	25	24	7	23-
9	25	26	25-	8-
L= 2 H= 10				
0	20	17	17	0
1	28	28	25	14-
2	31	30	30	5-
3	12	8	1	8
4	17	18	18-	4
5	15	15	15	4-
6	28	31	10-	30-
7	17	15	13-	7
L= 2 H= 11				
0	32	37	37-	0
1	10	16	11	11-
2	31	38	29-	24
3	28	38	27-	27-
L= 3 H= 0				
1	27	30	0	30-
2	12	11	11-	0
3	376	390	0	390
4	136	142	142	0
5	23	20	0	20-

Table 6. Continued.

6	56	62	62-	0
7	24	21	0	21-
8	34	31	31	0
9	82	81	0	81-
10	64	61	61	0
11	46	47	0	47
12	14*	0	0	0
13	58	53	0	53-
14	19	14	14	0
	L= 3 H= 1			
0	22	20	0	20-
1	287	321	263	183
2	200	235	161-	172-
3	121	142	115	84-
4	129	144	44	137-
5	113	122	102	67
6	28	25	9	24-
7	101	108	97-	49-
8	61	61	21-	58-
9	119	126	85	93
10	63	59	56-	19
11	36	29	24-	18-
12	41	38	32-	19-
13	27	27	12	25
14	34	34	20	28-
	L= 3 H= 2			
0	27	26	0	26-
1	31	25	18-	18
2	121	128	108-	69-
3	142	154	107	111-
4	113	118	78	88-
5	111	122	56	108
6	18	18	15	9-
7	100	106	90	56
8	126	135	82	107-
9	115	113	113-	1
10	54	52	16-	50-
11	44	34	29	18-
12	36	33	4	32-
13	35	32	4-	31-
14	66	78	15	76-
	L= 3 H= 3			
0	134	136	0	136-
1	46	40	4	40-
2	122	111	110-	12
3	46	47	27	38-
4	31	29	28	8
5	67	67	62	26
6	189	193	189-	41
7	145	148	109	101
8	91	85	12-	84-
9	69	70	62-	33
10	21	20	10-	18
11	23	20	6-	20-
12	24	20	9-	18-
13	58	67	61-	27
14	33	43	24-	35
	L= 3 H= 4			
0	60	61	0	61
1	155	168	129	108
2	101	99	99	6-
3	110	112	30	108-
4	135	148	3-	148-
5	47	45	41-	19-
6	58	56	40-	39-
7	60	61	39	47
8	142	139	25-	137-
9	52	47	31	35
10	47	38	18	34-
11	22	16	6	15
12	64	65	8	65-
13	22	18	9	16-
	L= 3 H= 5			
0	166	169	0	169
1	78	67	67-	1-
2	80	82	70-	43-
3	123	123	34-	118
4	121	118	53-	106
5	30	21	16	14
6	95	97	77-	58-
7	44	42	20-	37-
8	104	105	32-	100
9	68	67	61-	28
10	11*	5	3-	5-
11	43	40	33	22
12	16	14	13-	6-
13	30	39	6	39
	L= 3 H= 6			
0	21	18	0	18
1	17	16	4-	15
2	94	94	6	94-
3	94	96	84	46
4	125	129	52-	118
5	39	27	4-	27-
6	75	71	42	58-
7	18	16	15	3
8	61	54	26-	47-
9	36	34	8	34-
10	36	37	11-	35-
11	11	7	5	6
12	39	48	35-	32-
	L= 3 H= 7			
0	15*	8	0	8-
1	44	45	7	44-
2	96	97	41	88
3	86	86	86-	5
4	34	31	19-	24
5	91	91	89-	22
6	48	48	1	48
7	39	32	17-	27-
8	39	40	39-	2-
9	47	48	34	34
10	29	29	15-	25
11	14	15	8	12-
	L= 3 H= 8			
0	31	35	0	35
1	43	34	3-	34-
2	45	40	39-	9
3	17	14	13	5
4	19	15	15-	1-
5	21	19	19-	5-
6	15	16	7-	15
7	36	34	13	31-
8	49	48	5	48
9	27	31	25	18
	L= 3 H= 9			
0	38	34	0	34
1	96	100	77-	64-
2	40	40	5-	40
3	22	21	18	12
4	32	30	9	29-
5	23	22	2	22-
6	12	13	6-	11
7	16	19	0	19
8	33	42	37	20
	L= 3 H= 10			
0	9*	3	0	3
1	51	59	28-	52-
2	48	53	16	50
3	8*	3	0	3
4	7*	1	0	1
5	14	19	7	17-
	L= 4 H= 0			
1	21	20	0	20
2	101	120	120-	0
3	92	102	0	102
5	39	41	0	41
6	22	17	17	0
7	78	82	0	82
8	53	54	54-	0
9	125	124	0	124-
10	32	30	30-	0
11	15*	11	0	11-
12	15	10	10	0
13	30	29	0	29-
	L= 4 H= 1			
0	14	16	16	0
1	31	30	30-	4-
2	132	161	151-	57
3	36	38	14-	36
4	90	94	47-	81-
5	101	103	77-	68
6	35	30	19-	23
7	127	135	114-	73-
8	35	27	11	25-
9	111	117	110-	41
10	43	36	10-	35
11	13	12	4	12
12	15	14	8	12
13	51	63	38-	51
	L= 4 H= 2			
0	26	26	26	0
1	96	99	55	82
2	56	50	1	50
3	124	141	135-	41
4	149	173	132-	112-
5	76	73	73	9-
6	49	45	1	45-
7	39	35	35	1-
8	52	45	21-	40-
9	63	66	63	19-
10	53	57	41	39-
11	44	47	32-	34-
12	56	58	35-	46
13	15	19	11	16
	L= 4 H= 3			
0	91	86	86-	0
1	103	107	59	89
2	155	169	166-	31-
3	159	174	173-	21-
4	140	145	144-	12
5	30	27	18-	21
6	68	58	23-	53
7	19	13	10	8
8	82	81	79-	15-
9	94	102	10	102
10	52	46	32	33-
11	23	23	23-	0
12	11*	4	0	4-
	L= 4 H= 4			
0	44	40	40	0
1	31	32	13	29
2	41	40	38-	15
3	128	128	125	26
4	157	164	117	115-
5	81	72	26-	68-
6	38	33	33-	5
7	38	35	5-	35-
8	53	53	11-	52-
9	61	61	3	61
10	38	35	7-	35-
11	23	25	25	0
12	17	19	14	13-
	L= 4 H= 5			
0	92	92	92-	0
1	36	34	6	33-
2	131	137	136-	7
3	64	56	49	27
4	62	52	41-	32
5	77	83	22-	80
6	70	67	30-	60-
7	82	86	81	28
8	72	69	64-	25
9	24	28	22-	18-
10	9*	4	3-	3
11	17	19	11	16
	L= 4 H= 6			
0	54	49	49	0
1	95	98	55-	82-
2	52	48	2	48-
3	19	14	5-	13
4	54	50	43	24-
5	42	38	38	2
6	16	12	11	4-
7	35	36	4-	35
8	49	49	46	16-
9	14	14	14	1
10	16	19	8	18-
	L= 4 H= 7			
0	18	14	14-	0
1	38	37	26	25
2	66	66	57-	33-
3	83	76	74	20-
4	33	27	26	8-
5	38	39	39	7-
6	40	41	31-	26
7	21	16	9	13-
8	13	10	10	1
9	25	31	27	14-
	L= 4 H= 8			
0	11*	1	1-	0
1	44	45	36-	27-
2	67	63	63	0
3	44	49	30	38-
4	41	39	39-	0
5	43	48	39-	27
6	27	28	28	1
7	9	10	9-	5-
	L= 4 H= 9			
0	14*	14	14	0
1	32	32	32-	7
2	59	74	58	46
3	25	30	15	26-
4	11	19	18-	6
5	27	39	33	21-
	L= 5 H= 0			
1	12	11	0	11
2	11	13	13-	0
3	61	49	0	49-
4	16	10	10-	0
5	61	60	0	60-
6	107	111	111	0
7	21	16	0	16-
8	50	53	53	0
9	45	45	0	45
10	52	55	55	0
11	30	36	0	36-
	L= 5 H= 1			
0	25	30	0	30-
1	80	86	63-	59-
2	36	34	27	21-
3	72	67	14-	66
4	11*	7	3-	6-
5	28	21	13	16
6	27	28	15	23-
7	72	64	51	39
8	32	25	25	2
9	55	60	34-	49-
10	48	50	46-	19
11	15	15	14	4
	L= 5 H= 2			
0	217	182	0	182-
1	168	160	135	85-
2	108	103	77	68
3	49	45	43	15
4	40	35	29	20
5	80	63	44	45-
6	50	39	24	31
7	26	22	11-	18
8	25	16	10	12
9	59	62	61	7-
10	37	41	40	10-
11	18	24	4	23-
	L= 5 H= 3			
0	36	36	0	36-
1	42	36	14	33
2	127	115	113	23-
3	52	45	13-	43
4	32	25	12-	21-
5	84	79	76-	22
6	38	32	23	22
7	15	13	11-	6
8	45	40	1	40
9	58	60	52	30
10	23	26	14-	22-
	L= 5 H= 4			
0	15*	7	0	7-
1	65	53	53	6
2	34	27	23-	15
3	114	104	90	52
4	33	27	24	13-
5	98	106	102	27
6	48	44	6	44-
7	86	95	38	87-
8	82	88	1-	88
9	10*	14	13	5
10	28	38	37-	6
	L= 5 H= 5			
0	55	42	0	42-
1	45	37	36-	9
2	67	56	14-	54
3	77	65	51	41-
4	41	37	29-	23-
5	51	49	41-	27
6	75	82	82	8
7	34	41	4-	40
8	39	46	19	42-
9	21	25	16-	19
	L= 5 H= 6			
0	40	33	0	33-
1	54	52	52	4
2	44	38	30-	24
3	53	46	14	43-
4	47	52	43-	30-
5	46	50	16	47
6	38	42	36-	21
7	31	36	35	9-
8	7*	8	7-	4
	L= 5 H= 7			
0	67	70	0	70
1	25	31	2	31
2	13*	6	4-	5-
3	13	9	2-	9
4	18	15	11	9
5	14	17	12	12
6	25	35	20	29-
	L= 5 H= 8			
0	17	18	0	18
1	9	11	8-	7-
2	12	21	10	19-
3	8*	6	6-	0
4	16	23	22-	4-

investigation of β-DL-arabiose by three-dimensional methods.[10] Furthermore, bond lengths in α-glucose from a neutron diffraction study of the compound [12] are given in the table. The latter values are probably the most reliable and the most representative for the C – C and C – O bond lengths in pyranoses.

Average bond lengths, mentioned below, are based on the values in Table 5, and weights inversely proportional to the respective standard deviations.

The anomeric C – O bond. The lengths found for the C(1) – O(1) bond in β-arabinose, α-xylose, and β-lyxose (*cf.* Table 5) are 1.382(12) and 1.392(4), 1.393(6), and 1.364(6) Å, respectively. This C – O bond is in each case the shortest C – O bond in the molecule, and it has probably somewhat different bonding environment than the others. C(1), in fact, is the only carbon atom bonded to two oxygens, O(1) and O(5).

The length of the C(1) – O(1) bond in β-arabinose and in α-xylose agree within one standard deviation with the C(1) – O(1) bond length, 1.389(6) Å, in α-glucose (Table 5). The difference between the latter and the C(1)–O(1) bond length in β-lyxose is 0.025 Å, or 4σ. It has been suggested elsewhere,[11] that this difference may be related to hybridization effects.[13] One should, in this context, also be aware that the anomeric C–O bond in β-lyxose is equatorial, while in β-arabinose, α-xylose, and α-glucose, it is axial.

The C–O(hydroxyl) bonds. The average length of the C–O(hydroxyl) bonds in β-arabinose, α-xylose, and β-lyxose, is 1.421 Å, as compared with the value 1.418 Å for the average length of equivalent bonds in α-glucose. The C(2)–O(2) bond length in β-arabinose, 1.454(8) Å from the two-dimensional study, and the C(2)–O(2) bond length in β-lyxose, differ by more than three standard deviations from the average length.

The cyclic C–O bonds are somewhat longer than the C–O(hydroxyl) bonds. From the X-ray studies (Table 5), the average length of the former bonds is 1.435 Å, and from the neutron study, it is 1.427 Å. There are no deviations greater than 3σ from the respective average lengths.

The values found for the C(1)–O(5)–C(5) angle in the different compounds may be mentioned in this connection. They are 112.4(3) in α-xylose, 113.8(4) in β-lyxose, 112.7(6) in β-arabinose, and 113.4(3)° in β-DL-arabinose. The average of these values, with weights inversely proportional to the respective standard deviations, is 113.1°, as compared with the value 113.8(2)° found for the C(1)–O(5)–C(5) angle in α-glucose.[12]

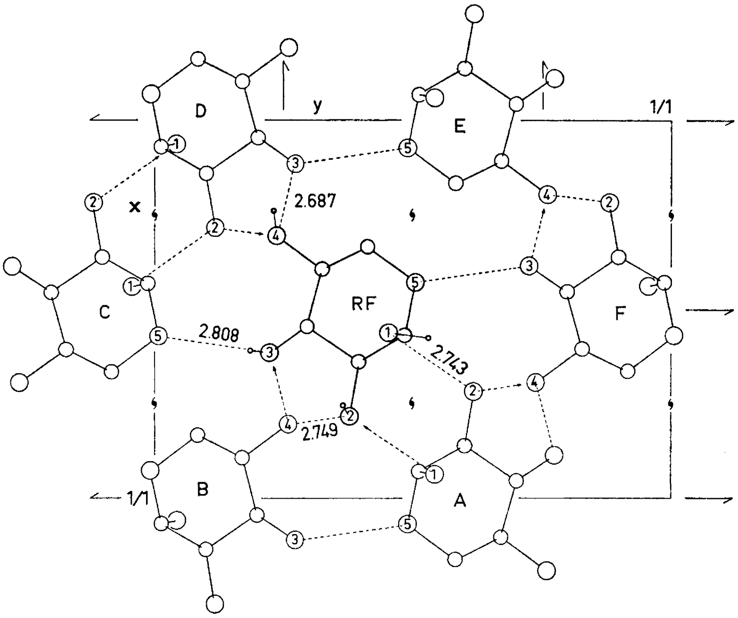


Fig. 2. The arrangement of α-xylose molecules in the crystal, as seen along the *c*-axis. The small circles indicate hydrogen atoms, and the arrows indicate that the atoms pointed at are situated one cell above or below. Atomic distances are given in Å units.

The $C-C$ bonds in β-arabinose, β-xylose, and α-lyxose range from 1.503 to 1.554 Å (*cf.* Table 5). Their average length is 1.526 Å as compared with the average length, 1.527 Å, for the equivalent bonds in α-glucose. A $C(sp^3)-C(sp^3)$ bond length of 1.526(2) Å has been proposed by Lide.[14]

The crystal structure. The arrangement of α-xylose molecules in the crystal, as seen along the c-axis, is shown in Fig. 2. Intermolecular $O\cdots O$ distances which correspond to hydrogen bonds are shown in the figure. The positions of the molecules $A-F$ relative to the position (x, y, z) of the reference molecule RF are the following:

A	$1.5-x$	$1.0-y$	$0.5+z$
B	$0.5+x$	$0.5-y$	$1.0-z$
C	$1.0-x$	$-0.5+y$	$0.5-z$
D	$-0.5-x$	$0.5-y$	$-z$
E	$0.5-x$	$1.0-y$	$-0.5+z$
F	$1.0-x$	$1.5-y$	$0.5-z$

There is a hydrogen bond, 2.743(5) Å, between O(1) of the reference molecule and O(2) of molecule A (Fig. 2). O(1) of A, in turn, forms a hydrogen bond to O(2) of the molecule one cell above RF, thus giving rise to a helix of molecules about the screw axis in $x=\frac{3}{4}$, $y=\frac{1}{2}$. An equivalent helix is found about the screw axis in $x=\frac{1}{4}$, $y=0$.

O(2) of the reference molecule forms a hydrogen bond, 2.749(5) Å, to O(4) of molecule B, O(3) forms one of 2.808(5) Å to O(5) of molecule C, and O(4) forms one of 2.687(5) Å to O(3) of molecule D. Thus, each of the atoms O(2), O(3), and O(4), accepts and donates a hydrogen bond (Fig. 2). O(5) accepts a hydrogen bond, and O(1) donates one.

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