Acta Cryst. (1975). B31, 862

The Crystal and Molecular Structure of *O*-(β-D-Xylopyranosyl)-L-serine and its Copper(II) Complex

BY LOUIS T. J. DELBAERE,* BORIS KAMENAR† AND KEITH PROUT

Chemical Crystallography Laboratory, Oxford University, 9 Parks Road, Oxford OX1 3PD, England

(*Received* 18 *October* 1974; *accepted* 2 *November* 1974)

The crystal structures of *O*-(β-D-xylopyranosyl)-L-serine (monoclinic $a=6{\cdot}05$, $b=9{\cdot}53$, $c=9{\cdot}43$ Å, $\gamma=94{\cdot}5°$; space group $P2_1$, Mo $K\alpha$ radiation, linear diffractometer data, 907 independent reflexions, final R 0·058) and bis-[*O*-(β-D-xylopyranosyl)-L-serinato]copper(II) (tetragonal $a=9{\cdot}82$, $c=21{\cdot}28$ Å; space group $P4_32_12$, Mo $K\alpha$ radiation, linear diffractometer data, 733 independent reflexions, final R 0·093) have been determined and refined by the full-matrix least-squares method. The dimensions and conformation of the molecules are discussed.

The carbohydrate–peptide bond in a number of complex macromolecules, *e.g.* heparin, chondroitin sulphates, is known to consist of a β-*O*-glycoside between xylose and serine (xyl-ser) (Lindahl & Roden, 1965). Xyl-ser has been synthesised by Lindberg & Silvander (1965), Derevitskaya, Vafina & Kochetkov (1967) and Higham, Kent & Fisher (1968).

The β-configuration of the glycosidic bond was assigned from nuclear magnetic resonance data from chromatographically pure, crystalline xyl-ser (in D_2O at 100 Hz) (Delbaere, Higham, Kamenar, Kent & Prout, 1972) who also reported the alkaline degradation of xyl-ser and the catalysis of this degradation by copper(II). The structures of xyl-ser and its copper complex were determined to study the conformation of xyl-ser and the effect of coordination with copper(II). These structures have appeared in a preliminary report (Delbaere *et al.*, 1972).

Experimental

Preparations

Crystals of xyl-ser and its copper complex were supplied by Dr P. W. Kent.

Structure analysis

For each compound preliminary cell dimensions and the space group were determined from Weissenberg and precession photographs. The cell dimensions were refined and X-ray intensities measured on a linear diffractometer with Mo $K\alpha$ radiation and balanced filters (xyl-ser: 907 independent reflexions, layers 0–5*kl* of a crystal $0{\cdot}5\times0{\cdot}2\times0{\cdot}25$ mm mounted about **a**; copper xyl-ser: 733 independent reflexions, layers 0–8*kl* of a crystal mounted about **a**) and corrected for Lorentz and polarization effects. Absorption corrections were not applied.

Crystal data

(*a*) *O*-(β-D-Xylopyranosyl)-L-serine (xyl-ser), $C_8H_{15}NO_7$, $M=237{\cdot}22$, monoclinic, $a=6{\cdot}05$ (2), $b=9{\cdot}53$ (3), $c=9{\cdot}43$ (3) Å, $\gamma=94{\cdot}5$ (2)°, $D_m=1{\cdot}47$ g cm^{-3}, $Z=2$, $D_c=1{\cdot}453$ g cm^{-3}, space group $P2_1$ (C_2^2, No. 4 first setting), systematic extinctions $00l$, $l=2n+1$; Mo $K\alpha$ radiation $\mu=1{\cdot}38$ cm^{-1}.

(*b*) Bis-[*O*-(β-D-xylopyranosyl)-L-serinato]copper(II) (copper xyl-ser), $C_{16}H_{28}N_2O_{14}Cu$, $M=535{\cdot}94$, tetragonal, $a=9{\cdot}82$ (3), $c=21{\cdot}28$ (4) Å, $D_m=1{\cdot}70$ g cm^{-3}, $Z=4$, $D_c=1{\cdot}736$ g cm^{-3}, space group $P4_32_12$ (D_4^8, No. 96) systematic extinctions $h00$, $h\neq2n$, $00l$, $l\neq4n$; Mo $K\alpha$ radiation, $\mu=2{\cdot}49$ cm^{-1}.

The structure xyl-ser was determined by direct methods. The reflexions 120, 370 and 521 were fixed at 0 to define the origin. $\sum_1$ relationships indicated that the phase of 040 was π and $\sum_2$ relationships that if the phase of 237 was a then that of $2\bar{1}12$ would be $2a$; a was given the value $\pi/4$ and application of the tangent formula gave phases for a set of E's that yielded an E map in which the 16 largest peaks corresponded to the xyl-ser molecule. The trial model was refined by the full-matrix least-squares method first with isotropic then anisotropic temperature factors. Hydrogen atoms were found from a difference map at $R=0{\cdot}066$ but not refined. The refinement converged after six cycles at $R=0{\cdot}058$. Unit weights were used.

The structure of copper xyl-ser was determined by the heavy-atom method. The trial structure obtained was refined by full-matrix least-squares calculations with isotropic temperature factors. The F_o map at $R=0{\cdot}156$ showed C(3) partially resolved into two maxima and O(3) clearly resolved into two well separated peaks. These atoms and C(2), O(2), C(4) and O(4) all had anomalously high temperature factors, but all atoms other than O(3) and C(3) were clearly resolved single maxima. The F_o map was compatible with a mixture of two β-chair forms, one with the pyranose ring much flatter than the other. The refinement proceeded on the assumption that the crystal con-

* Present address: Department of Biochemistry, University of Alberta, Edmonton 7, Alberta, Canada.

† On leave from the University of Zagreb, Yugoslavia.

Table 1. *O-(β-D-Xylopyranosyl)-L-serine: final atomic positional and thermal parameters (hydrogen atoms × 10^3 and 10^2, others × 10^4 and 10^3 respectively) with standard deviations in parentheses*

The temperature factor T is given by $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	6552 (10)	7119 (6)	4058 (6)	58 (5)	27 (3)	22 (3)	−4 (3)	3 (3)	−5 (2)
C(2)	4332 (11)	7509 (6)	3565 (6)	53 (4)	26 (3)	18 (3)	1 (2)	2 (2)	4 (2)
C(3)	4356 (12)	7706 (6)	1953 (7)	61 (5)	35 (3)	25 (3)	10 (3)	1 (3)	3 (3)
C(4)	5072 (13)	6350 (6)	1281 (6)	67 (5)	32 (3)	17 (3)	−4 (3)	0 (3)	−4 (2)
C(5)	7246 (14)	5957 (7)	1884 (7)	80 (6)	50 (4)	21 (3)	18 (3)	−1 (4)	−1 (3)
C(6)	8568 (12)	7062 (6)	6242 (6)	55 (5)	19 (3)	24 (3)	9 (3)	−4 (3)	−4 (2)
C(7)	8871 (10)	8546 (5)	6864 (6)	38 (4)	28 (3)	19 (2)	−4 (2)	−2 (2)	−1 (2)
C(8)	11124 (11)	8710 (6)	7640*	45 (5)	42 (3)	25 (3)	−3 (3)	−7 (3)	3 (3)
O(1)	7110 (9)	5816 (4)	3425 (4)	75 (4)	37 (2)	21 (2)	14 (2)	−4 (2)	−4 (2)
O(2)	3779 (9)	8767 (4)	4208 (5)	102 (4)	36 (2)	27 (2)	28 (2)	12 (3)	3 (2)
O(3)	2281 (11)	8039 (6)	1544 (5)	98 (5)	77 (4)	26 (2)	35 (3)	−7 (3)	11 (2)
O(4)	5355 (9)	6539 (5)	−228 (5)	88 (4)	43 (2)	18 (2)	−12 (2)	0 (2)	0 (2)
O(6)	6449 (8)	6878 (4)	5524 (4)	52 (3)	31 (2)	18 (2)	−5 (2)	−4 (2)	−3 (2)
O(8)	12782 (8)	8557 (6)	6914 (5)	42 (3)	103 (4)	25 (2)	−2 (3)	2 (2)	−0 (3)
O(9)	11076 (9)	8961 (6)	8962 (6)	62 (4)	90 (4)	20 (2)	8 (3)	−7 (2)	−7 (2)
N(1)	7030 (9)	8770 (5)	7855 (5)	43 (4)	32 (2)	27 (2)	−1 (2)	−2 (2)	1 (2)

tained equal amounts of the two forms with distinct sites for $C(3_1)$ and $C(3_2)$, $O(3_1)$ and $O(3_2)$. These atoms were given isotropic temperature factors, but the others anisotropic. All reflexions had unit weights. The refinement converged after five cycles at $R=0{\cdot}093$. The final difference map had no major features and hydrogen atoms could not be located.

All calculations, except those for phase determination, used J. M. Stewart's X-RAY 70 system adapted for the Oxford University 1906A computer. The phase determination was carried out on the KDF9 computer with a set of local programs. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The observed structure amplitudes and structure factors calculated from the final atomic parameters in Tables 1 and 3 are available.* Tables 2 and 4 record interatomic distances, and interbond and dihedral angles. The standard deviations were calculated from only the leading diagonal terms of the variance–covariance matrix and are probably underestimated.

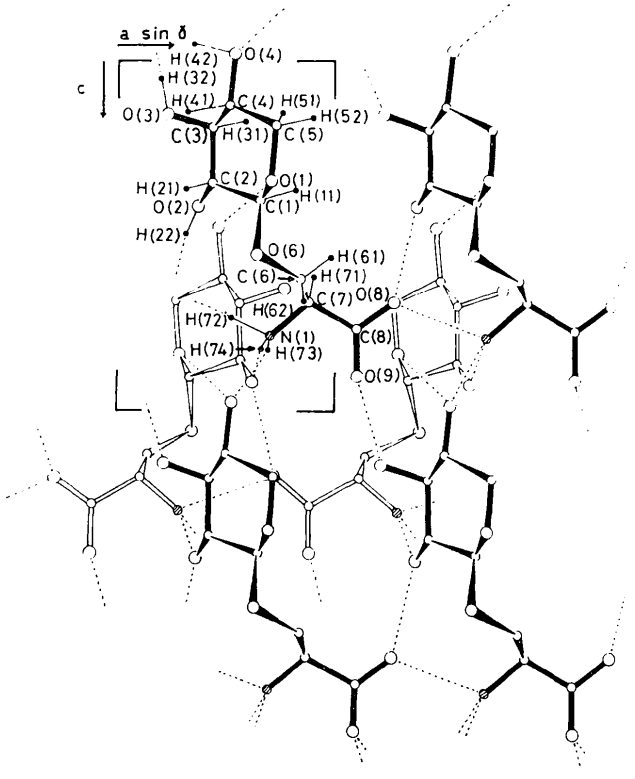

Fig. 1. The crystal structure of xyl-ser in projection down **b**.

Table 1 (*cont.*)

	x	y	z	U_{iso}
H(11)	813	787	375	7
H(21)	312	687	375	5
H(22)	313	850	500	10
H(31)	683	850	175	7
H(32)	188	813	50	10
H(41)	314	550	150	7
H(42)	354	612	−50	9
H(51)	750	500	150	9
H(52)	895	688	162	9
H(61)	980	700	563	6
H(62)	853	638	687	6
H(71)	896	925	613	5
H(72)	521	862	738	5
H(73)	708	812	837	5
H(74)	688	975	812	5

Discussion

The crystals of xyl-ser are built up from isolated xyl-ser molecules in the zwitterion form (Fig. 1). The molecules are linked by a complex hydrogen-bonded network such that all hydrogen atoms attached to oxygen or nitrogen take part in a hydrogen bond. Of the ni-

* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30762 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

trogen and oxygen atoms only O(6) of the xyl-ser ether linkage takes no part in the hydrogen bonding.

The β-configuration at the xylopyranose is confirmed. The ring has an almost ideal chair form as demonstrated by the dihedral angles, Table 2. The interatomic distances and interbond angles agree reasonably with those in α-xylopyranose (Hordvik, 1971) although the spread of values is greater than might have been expected, probably due to the relatively unfavourable parameter to observation ratio.

Table 2. *O-(β-D-Xylopyranosyl)-L-serine: interatomic distances* (Å), *interbond angles* (°) *and dihedral angles* (°)

C(1)–C(2)	1·497 (10)	C(1)–C(2)–C(3)	110·2 (5)
C(1)–O(1)	1·441 (7)	C(1)–C(2)–O(2)	110·9 (5)
C(1)–O(6)	1·406 (7)	O(2)–C(2)–C(3)	108·5 (5)
C(2)–O(2)	1·411 (7)	C(2)–C(3)–C(4)	107·6 (5)
C(2)–C(3)	1·533 (8)	C(2)–C(3)–O(3)	108·2 (6)
C(3)–O(3)	1·383 (10)	C(4)–C(3)–O(3)	113·9 (6)
C(3)–C(4)	1·531 (9)	C(3)–C(4)–C(5)	111·6 (5)
C(4)–O(4)	1·444 (7)	C(3)–C(4)–O(4)	109·9 (5)
C(4)–C(5)	1·506 (11)	O(4)–C(4)–C(5)	107·7 (6)
C(5)–O(1)	1·463 (8)	C(4)–C(5)–O(1)	110·6 (6)
O(6)–C(6)	1·440 (8)	C(1)–O(1)–C(5)	110·5 (5)
C(6)–C(7)	1·531 (8)	C(1)–O(6)–C(6)	114·6 (5)
C(7)–N(1)	1·487 (8)	O(6)–C(6)–C(7)	109·5 (5)
C(7)–C(8)	1·531 (9)	C(6)–C(7)–C(8)	108·7 (5)
C(8)–O(8)	1·235 (8)	C(6)–C(7)–N(1)	109·6 (5)
C(8)–O(9)	1·267 (5)	N(1)–C(7)–C(8)	110·7 (4)
C(2)–C(1)–O(1)	110·6 (5)	C(7)–C(8)–O(8)	116·7 (3)
C(2)–C(1)–O(6)	108·6 (5)	C(7)–C(8)–O(9)	117·3 (6)
O(1)–C(1)–O(6)	106·2 (4)	O(8)–C(8)–O(9)	126·1 (6)

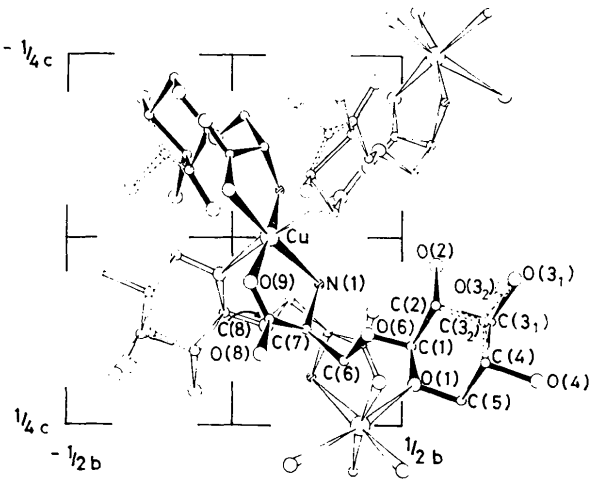

Fig. 2. Crystal structure of copper xyl-ser in projection down **a**.

Table 2 (*cont.*)

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

O(1)···H(42)–O(4^{i})	2·887 (6)	O(8)···H(72)–N(1^{ii})	2·713 (7)
O(8)···H(22)–O(2^{ii})	2·636 (7)	N(1)–H(73)···O(4^{iv})	2·908 (7)
O(9)···H(32)–O(3^{iii})	2·696 (7)	N(1)–H(74)···O(2^{v})	2·746 (7)
Dihedral angles*			
O(1)–C(1)–C(2)–O(2)	−62·7°	O(6)–C(6)–C(7)–N(1)	−58·2
O(1)–C(1)–O(6)–C(6)	−95·2	O(6)–C(6)–C(7)–C(8)	−179·3
C(2)–C(1)–O(6)–C(6)	156·2	C(6)–C(7)–C(8)–O(9)	118·9
C(1)–O(6)–C(6)–C(7)	−84·2	N(1)–C(7)–C(8)–O(9)	1·5

* In Table 2 and Table 4 the dihedral angle about the bond *J–K* is the angle the bond *K–L* is rotated from the *IJK* plane. It is positive when on looking from *IJ* to *KL* the rotation is clockwise.

Table 3. *Bis-[O-(β-D-xylopranosyl)-L-serinato]copper(II): final atomic positional* ($\times 10^4$) *and thermal parameters* ($\times 10^3$) *with standard deviations in parentheses*

The temperature factor is given by $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

	x/a	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	11125 (2)	1124*	0*	24 (6)	56 (7)	67 (2)	−9 (1)	0*	0*
C(1)	9078 (15)	5339 (13)	1422 (10)	27 (8)	16 (6)	86 (13)	4 (6)	−4 (9)	−9 (8)
C(2)	8443 (20)	5980 (18)	889 (10)	82 (14)	38 (9)	58 (12)	19 (9)	−3 (9)	−7 (10)
C(3$_1$)	8558 (42)	7551 (36)	1075 (18)	46 (9)					
C(3$_2$)	7825 (37)	7475 (31)	1079 (16)	35 (7)					
C(4)	7326 (19)	7522 (18)	1632 (11)	54 (11)	34 (9)	96 (18)	11 (8)	−8 (11)	−4 (10)
C(5)	8055 (20)	6760 (18)	2165 (11)	73 (13)	41 (10)	68 (15)	7 (9)	8 (11)	−15 (10)
C(6)	10354 (21)	3333 (18)	1635 (11)	73 (13)	44 (10)	62 (14)	18 (9)	−10 (10)	−17 (9)
C(7)	10883 (18)	2191 (15)	1230 (9)	52 (10)	40 (9)	51 (12)	10 (7)	−1 (9)	11 (8)
C(8)	9750 (19)	1087 (8)	1109 (11)	69 (12)	25 (8)	75 (16)	19 (9)	37 (11)	17 (11)
O(1)	8171 (14)	5368 (11)	1952 (7)	80 (9)	29 (6)	66 (10)	−2 (6)	16 (8)	5 (6)
O(2)	9207 (19)	5926 (16)	347 (9)	150 (16)	68 (10)	84 (12)	35 (11)	30 (11)	−5 (9)
O(3$_1$)	8089 (29)	8331 (28)	513 (15)	71 (7)					
O(3$_2$)	6818 (27)	7856 (26)	626 (15)	64 (7)					
O(4)	7171 (13)	8950 (14)	1883 (10)	56 (8)	40 (7)	147 (16)	22 (7)	18 (9)	3 (9)
O(6)	9295 (10)	3958 (12)	1283 (6)	42 (6)	37 (6)	77 (9)	17 (5)	−16 (6)	−8 (7)
O(8)	8965 (18)	871 (11)	1543 (8)	113 (12)	23 (7)	108 (12)	3 (7)	42 (12)	−1 (7)
O(9)	9738 (11)	553 (10)	579 (7)	40 (7)	33 (6)	75 (10)	−14 (5)	20 (6)	−20 (6)
N(1)	11404 (11)	2606 (11)	624 (7)	27 (7)	26 (6)	60 (10)	−11 (5)	−6 (6)	−4 (6)

Table 4. *Bis*-[*O*-(β-D-*xylopyranosyl*)-L-*serinato*]*copper*-(II): *interatomic distances* (Å), *interbond angles* (°) *and dihedral angles* (°)

(i) $\frac{3}{2}+y,\frac{3}{2}-x,\frac{1}{4}+z$; (ii) $2-x,\frac{1}{2}+y,-\frac{1}{4}-z$; (iii) $1+y,x-1,-z$.

Cu—N(1)	1·99 (1)	N(1)—Cu–N(1^{iii})	104·1 (5)
Cu—O(9)	1·92 (1)	O(9)—Cu–O(9^{iii})	90·1 (4)
Cu—O(1)	2·75 (1)	O(1^{ii})–Cu–O(1^{i})	164·0 (6)
N(1)–Cu–O(9)	83·2 (5)	O(9)—Cu–N(1^{iii})	170·9 (6)
N(1)–Cu–O(1^{i})	79·9 (5)	N(1)—Cu–O(1^{ii})	90·3 (5)
O(1^{i})–Cu–O(9)	96·4 (4)	O(9)—Cu–O(1^{ii})	94·9 (4)
C(1) –C(2)	1·42	C(1) –C(2) –O(2)	116
C(1) –O(1)	1·43	O(2)–C(2) –$C(3_1)$	104
C(1) –O(6)	1·41	O(2)–C(2) –$C(3_2)$	117
C(2) –O(2)	1·36	C(2) –$C(3_1)$–C(4)	97
C(2) –$C(3_1)$	1·63	C(2) –$C(3_2)$–C(4)	117
C(2) –$C(3_2)$	1·60	C(2) –$C(3_1)$–$O(3_1)$	107
$C(3_1)$–$C(3_1)$	1·45	C(2) –$C(3_2)$–$O(3_2)$	113
$C(3_2)$–$O(3_2)$	1·43	C(4) –C(3) –$O(3_1)$	115
$C(3_1)$–C(4)	1·65	C(4) –$C(3_2)$–$O(3_2)$	109
$C(3_2)$–C(4)	1·29	$C(3_1)$–C(4) –C(5)	104
C(4) –O(4)	1·51	$C(3_2)$–C(4) –C(5)	118
C(4) –C(5)	1·54	$C(3_1)$–C(4) –O(4)	107
C(5) –O(1)	1·45	$C(3_2)$–C(4) –O(4)	116
O(6)–C(6)	1·42	O(4)–C(4) –C(5)	104
C(6) –C(7)	1·51	C(4) –C(5) –O(1)	105
C(7) –N(1)	1·45	C(1) –O(1)–C(5)	108
C(7) –C(8)	1·58	C(1) –O(6)–C(6)	115
C(8) –O(8)	1·22	O(6)–C(6) –C(7)	106
C(8) –O(9)	1·24	C(6) –C(7) –C(8)	112
C(2) –C(1)–O(1)	111	C(6) –C(7) –N(1)	115
C(2) –C(1)–O(6)	109	N(1)–C(7) –C(8)	107
O(1)–C(1)–O(6)	106	C(7) –C(8) –O(8)	116
C(1) –C(2)–$C(3_1)$	104	C(7) –C(8) –O(99)	117
C(1) –C(2)–$C(3_2)$	111	O(8)–C(8) –O(9)	128

(iv) $x,y-1,z$; (v) $x-\frac{1}{2},\frac{1}{2}-y,\frac{1}{4}-z$; (vi) $x-\frac{1}{2},\frac{3}{2}-y,\frac{1}{4}-z$; (vii) $y,x,-z$.

Hydrogen bonds

O(9)···$O(3_1^{iv})$	2·72	O(4)···$O(2^{iv})$	2·98
O(8)···$N(1^{v})$	3·00	O(2)···$O(3_2^{vii})$	2·61
O(8)···$O(4^{iv})$	2·67		

Dihedral angles

O(1)–C(1)–O(6)–C(6)	−94	O(6)–C(6)–C(7)–C(8)	−63
C(2)–C(1)–O(6)–C(6)	154	C(6)–C(7)–C(8)–O(9)	144
C(1)–O(6)–C(6)–C(7)	−153	N(1)–C(7)–C(8)–O(9)	17
O(6)–C(6)–C(7)–N(1)	60		

The five atoms of the amino-acid functional group are coplanar within experimental error with some barely significant asymmetry in the carboxylate group. The linkage O(6)–C(6)–C(7)–C(8) is *trans* (dihedral angle −179·3°) and the plane of these four atoms is almost at right-angles to the O(6)–C(1) bond. The linkage C(6)–O(6)–C(1)–H(11) has, approximately, the *cis* conformation and the C(1)–O(1) bond is almost at right angles to the C(6)–O(6)–C(1) plane. The conformation of the molecule is that required to minimize the repulsion between the hydrogen atoms attached to the skeleton of the molecule.

In the copper complex (Fig. 2) each Cu has an irregular octahedral coordination with crystallographic symmetry. The coordination sphere is formed from four different xyl-ser ligands. Two of these ligands form a planar *cis* amino acid chelate system in which Cu–N and Cu–O are 1·99 and 1·92 Å respectively, in good agreement with those found in other amino acid chelates (Freeman, 1967) as is the N–Cu–O angle in the chelate ring. The CuN_2O_2 group is planar but the N–Cu–N angle, 104·1°, is much larger than the O–Cu–O angle possibly due to the mutual repulsions of the amino-hydrogen atoms. The fifth and sixth positions of the coordination sphere are taken by the cyclic ether oxygen atoms of two other xyl-ser ligands to form long, 2·75 Å, Cu–O contacts.

Within experimental error there is reasonable agreement between the dimensions of the ligand and those found for free xyl-ser but the conformation of the ligand is modified to accommodate the copper coordination.

The major changes are in the O(6)–C(6)–C(7)–C(8) system which, instead of being *trans* coplanar as in xyl-ser, has a dihedral angle of −63° and in the C(1)–O(6)–C(6)–C(7) group which in the ligand approaches the *trans* coplanar configuration (dihedral angle −153°) whereas in xyl-ser the C(7)–C(6) is almost at right angles to the O(6)–C(1) bond. The rest of the molecule is little changed. The amino acid group is significantly less planar. The two slightly different chair forms of the β-xylopyranose are probably due to alternative possibilities for hydrogen bonding (Table 4).

We thank the National Research Council of Canada for a fellowship (for L.T.J.D.) and the S.R.C. (UK) for support.

References

DELBAERE, L. T. J., HIGHAM, M., KAMENAR, B., KENT, P. W. & PROUT, C. K. (1972). *Biochem. Biophys. Acta*, **286**, 441–444.

DEREVITSKAYA, V. A., VAFINA, M. A. & KOCHETKOV, N. K. (1967). *Carbohydr. Res.* **3**, 377–388.

FREEMAN, H. C. (1967). *Advanc. Protein Chem.* **22**, 257–424.

HIGHAM, M., KENT, P. W. & FISHER, D. (1968). *Biochem. J.* **108**, 47P.

HORDVIK, A. (1971). *Acta Chem. Scand.* **25**, 2175–2182.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

LINDAHL, U. & RODEN, J. (1965). *J. Biol. Chem.* **240**, 2821–2826.

LINDBERG, B. & SILVANDER, B. G. (1965). *Acta Chem. Scand.* **19**, 530–531.