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# The Molecular Structure of α-D-Talose

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Crystals of α-D-talose $C_6O_6H_{12}$ are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a=8.101(2)$ Å, $b=12.126(2)$ Å, $c=7.655(1)$ Å, and $Z=4$.

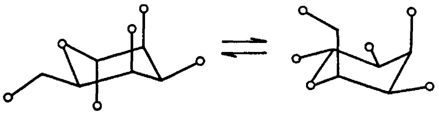
X-Ray intensity data were collected on a Siemens AED diffractometer using Mo*K*α radiation and the five-value scan technique. The structure was solved by direct methods and refined by full-matrix least squares.

α-Talose occurs in the conversion form 1*a*2*a*3*e*4*a*5*e*. The length of the anomeric C(1)–O(1) bond is 1.403(3) Å, and the C(1)–O(5)–C(5) angle is 113.7(2)° with C(1)–O(5) = 1.438(3) Å and C(5)–O(5) = 1.434(3) Å.

In the crystal there is a complete set of hydrogen bonds; O(2)···O(4) = 2.654(3) Å is intramolecular with H(O2)···O(4) = 1.96 Å.

An analysis of the standard deviations in the C–C and C–O bond lengths as a function of the intensity threshold value has been carried out. The standard deviations increase by a factor of 1.5 for a change in the threshold value from $\sigma(I)$ to $10\sigma(I)$. Corresponding values for $R$ are 0.078 and 0.026, and the numbers of reflections per parameter are 13.8 and 4.3, respectively.

The possible pyranose forms of α-D-talose are 1*a*2*a*3*e*4*a*5*e* (I) and 1*e*2*e*3*a*4*e*5*a* (II), II being formed from I through a conversion of the ring.



(I) (II)

A stability scheme for the conversion forms of pyranoses was proposed by Reeves in 1950,[1] and the normal conformation of a series of pyranoses have been correctly predicted from this scheme.

However, in the case of α-talose the difference in stability between forms I and II is too small for a prediction to be made, and a structure study of α-talose was therefore thought of interest.

Results from a preliminary X-ray investigation of α-D-talose have been reported.[2]

## STRUCTURE ANALYSIS

*Crystal data.*

α-D-Talose, $C_6O_6H_{12}$; M.W. = 180.16
Space group $P2_12_12_1$
$a=8.101(2)$ Å, $b=12.126(2)$ Å, $c=7.655(1)$ Å
$V=751.97$ Å$^3$
$D_c=1.591$ g/cm$^3$, $D_m$ (flotation) = 1.59 g/cm$^3$
$Z=4$
$\mu=1.55$ cm$^{-1}$ (Mo*K*α)

All the X-ray measurements were carried out on a papertape controlled Siemens AED diffractometer using Mo*K*α radiation ($\lambda=0.71069$ Å).

The unit cell dimensions were determined from the $2\theta$ values of 16 high order reflections measured at room temperature, $t=22$ °C. A least squares procedure gave the values quoted above.

The intensities of the reflections were measured by means of the five-value scan technique.[3] 2961 independent reflections were measured within $\theta=42°$.

Lp corrections were carried out in the usual way, but absorption corrections were considered unnecessary. The dimensions of the crystal used for the intensity collection were 0.2 × 0.3 × 0.4 mm in the three axial directions.

The scattering factors for oxygen and carbon were taken from the *International Tables*.[4] For hydrogen, the scattering factor curve given by Stewart *et al.*[5] was used.

*Table 1.* Atomic coordinates in fractions of corresponding cell edges. The standard deviations given in parentheses refer to the last digits of the respective values.

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| O(1) | 0.16055(25) | 0.11857(15) | −.07331(21) |
| O(2) | 0.04684(20) | 0.11688(14) | 0.38321(21) |
| O(3) | 0.13025(20) | 0.34071(13) | 0.34129(24) |
| O(4) | 0.35274(19) | 0.17603(14) | 0.46492(21) |
| O(5) | 0.31694(17) | 0.04293(11) | 0.15639(19) |
| O(6) | 0.67062(21) | 0.01932(15) | 0.07775(25) |
| C(1) | 0.15583(27) | 0.07540(18) | 0.09663(28) |
| C(2) | 0.08353(25) | 0.16380(17) | 0.21734(28) |
| C(3) | 0.20314(27) | 0.26040(16) | 0.23022(28) |
| C(4) | 0.37218(25) | 0.22088(17) | 0.29368(28) |
| C(5) | 0.43391(27) | 0.13315(17) | 0.16523(28) |
| C(6) | 0.59898(29) | 0.08400(21) | 0.21496(33) |
| H(11) | 0.0934(28) | 0.0088(17) | 0.1064(29) |
| H(21) | −.0189(25) | 0.1871(16) | 0.1706(26) |
| H(31) | 0.2167(25) | 0.2913(16) | 0.1171(26) |
| H(41) | 0.4447(27) | 0.2783(16) | 0.2977(26) |
| H(51) | 0.4395(28) | 0.1635(17) | 0.0521(27) |
| H(61) | 0.6712(32) | 0.1422(21) | 0.2385(33) |
| H(62) | 0.5936(31) | 0.0381(21) | 0.3238(36) |
| H(O1) | 0.1865(40) | 0.0741(25) | −.1324(41) |
| H(O2) | 0.1281(31) | 0.1187(21) | 0.4407(31) |
| H(O3) | 0.1909(33) | 0.3841(22) | 0.3601(36) |
| H(O4) | 0.4371(30) | 0.1836(19) | 0.5165(32) |
| H(O6) | 0.6072(33) | −.0076(21) | 0.0330(38) |

The structure was solved by direct methods (MULTAN)[6] and refined by full matrix least squares (see Ref. 7). All the hydrogen atoms were found from a difference map.

Final atomic coordinates and temperature parameters are listed in Tables 1 and 2, respectively. The values there correspond to the refinement in which $3\sigma(I)$ was used as intensity threshold value. With this criterion 1556 out of 2961 measured reflections were accepted as observed. The value of $R$ for this refinement is 0.047. The structure factor list is available on request.

The calculations mentioned above were carried out on a UNIVAC 1110 computer at the University of Bergen. The programs, with some exceptions, originate from the Weizmann Institute of Science, Rehovoth, Israel.

## DISCUSSION

The conversion form of α-D-talose in the crystalline state is l*a*2*a*3*e*4*a*5*e*, *cf.* Fig. 1. One may query, however, whether it is the assumed stabilizing effect of the axial hydroxyl group on C(1) that has been decisive for the structure

*Table 2.* Temperature parameters $U_{ij}$(Å$^2$) for oxygen and carbon, and $U$(Å$^2$) for hydrogen. The expressions used are $\exp\{-2\pi^2(h^2a^{*2}U_{11}+\cdots+2hka^*b^*U_{12}+\cdots)\}$ and $\exp\{-8\pi U(\sin^2\theta/\lambda^2)\}$. All values are multiplied by $10^4$. Standard deviations in parentheses refer to the last digits of the respective values.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{23}$ | $U_{13}$ |
|---|---|---|---|---|---|---|
| O(1) | 452(11) | 358(9) | 209(8) | 103(9) | −63(8) | −65(8) |
| O(2) | 240(8) | 303(9) | 276(9) | −48(7) | 37(7) | 28(7) |
| O(3) | 261(8) | 199(7) | 417(10) | −40(7) | −99(8) | 113(8) |
| O(4) | 247(8) | 376(9) | 216(8) | −70(8) | 36(7) | −59(7) |
| O(5) | 217(7) | 187(7) | 256(8) | 22(6) | −14(6) | −16(7) |
| O(6) | 231(8) | 315(9) | 413(1) | 55(8) | −70(8) | 8(8) |
| C(1) | 208(10) | 204(10) | 252(11) | 16(9) | −26(9) | −58(9) |
| C(2) | 175(9) | 192(10) | 233(10) | 12(8) | 12(9) | −12(8) |
| C(3) | 203(9) | 171(9) | 206(10) | −6(8) | −5(8) | 37(8) |
| C(4) | 174(9) | 182(9) | 229(10) | −49(8) | 16(8) | 12(8) |
| C(5) | 205(9) | 216(11) | 201(10) | 18(8) | 22(9) | 19(9) |
| C(6) | 197(10) | 277(12) | 309(13) | 30(9) | −21(10) | −17(10) |

| Atom | $U$ | Atom | $U$ | Atom | $U$ |
|---|---|---|---|---|---|
| H(11) | 153(58) | H(51) | 129(54) | H(O2) | 237(72) |
| H(21) | 31(47) | H(61) | 295(70) | H(O3) | 286(78) |
| H(31) | 71(50) | H(62) | 325(69) | H(O4) | 156(62) |
| H(41) | 75(51) | H(O1) | 519(108) | H(O6) | 287(90) |

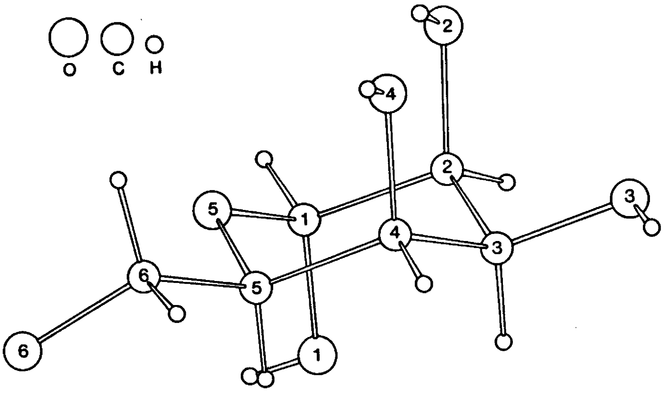


*Fig. 1.* The α-D-talose molecule with numbering of atoms.

in this case.[8] There is namely, in the present structure as well as in the structure of methyl-β-D-ribopyranoside,[9,10] methyl-1-thio-α-D-ribopyranoside[11] and methyl-1,5-dithio-β-D-ribopyranoside,[11] an intramolecular hydrogen bond between O(2) and O(4) which at least to some degree stabilizes the molecule. Thus, the possibility for such bonding should be taken into account when assessing the stabilities of the conversion forms of pyranoses. On the other hand, 5-thio-β-D-ribopyranoside occurs as 1*e*2*e*3*a*4*e* in the crystal,[12] showing that molecular packing too may be of importance for the choice of conversion form.

Bond lengths and angles in the α-D-talose molecule, as derived from the coordinates in Table 1, are listed in Table 3. It is realized that a more realistic estimate of the standard deviations probably might be obtained by multiplying those given by a factor of two.[13]

The values in Table 3 are normal for pyranose molecules. One notes that C(1) – O(1) = 1.403(3) Å is shorter than the other C – O bonds in the molecule and that C(1) – O(5) – C(5) = 113.7(2)° is greater than the other bond angles in the pyranose ring.

In the crystal there is a complete set of hydrogen bonds, *cf.* Fig. 2. The lengths

*Table 3.* Bond angles ∠(ijk) and bond lengths *D*(ij) in α-D-talose. The standard deviations are 0.2° in bond angles and 0.003 Å in bond lengths.

| i | j | k | ∠(ijk)° | i | j | *D*(ij) Å |
|---|---|---|---|---|---|---|
| C(2) | C(1) | O(1) | 108.0 | C(1) | C(2) | 1.532 |
| C(2) | C(1) | O(5) | 110.3 | C(2) | C(3) | 1.523 |
| O(1) | C(1) | O(5) | 111.9 | C(3) | C(4) | 1.530 |
| C(1) | C(2) | O(2) | 109.8 | C(4) | C(5) | 1.533 |
| C(1) | C(2) | C(3) | 109.5 | C(5) | C(6) | 1.513 |
| O(2) | C(2) | C(3) | 112.5 | C(1) | O(1) | 1.403 |
| C(2) | C(3) | O(3) | 107.5 | C(1) | O(5) | 1.438 |
| C(2) | C(3) | C(4) | 110.4 | C(2) | O(2) | 1.423 |
| O(3) | C(3) | C(4) | 113.4 | C(3) | O(3) | 1.421 |
| C(3) | C(4) | O(4) | 108.2 | C(4) | O(4) | 1.428 |
| C(3) | C(4) | C(5) | 107.8 | C(5) | O(5) | 1.449 |
| O(4) | C(4) | C(5) | 111.1 | C(6) | O(6) | 1.434 |
| C(4) | C(5) | O(5) | 109.9 | | | |
| C(4) | C(5) | C(6) | 113.6 | | | |
| C(6) | C(5) | O(5) | 107.0 | | | |
| C(5) | C(6) | O(6) | 112.9 | | | |

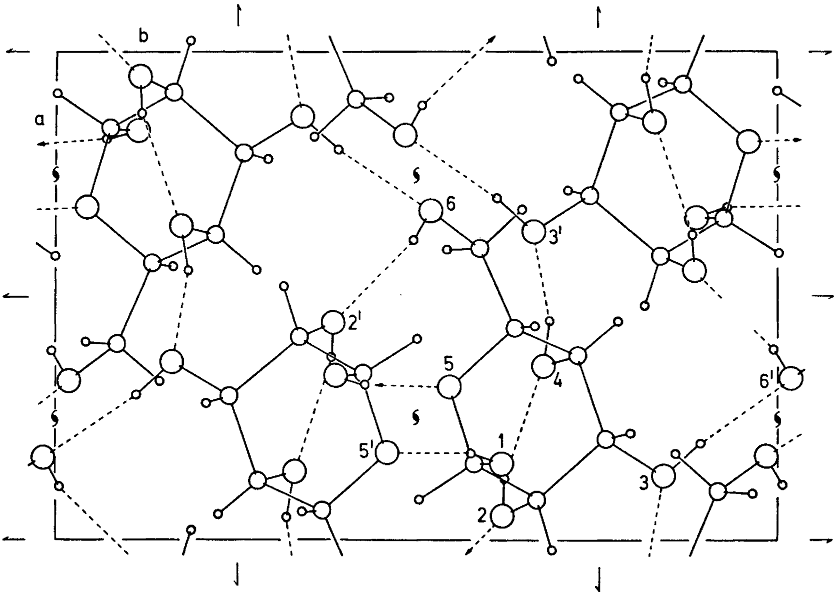


*Fig. 2.* The crystal structure of α-talose as seen along *c*. The O···H contacts in hydrogen bonds are indicated, and the oxygen atoms are numbered in accordance with the text.

of these are, O(1)···O(5)' = 2.855(3) Å, O(2)···O(4) = 2.654(3) Å (this hydrogen bond is intramolecular with H(O2)···O(4) = 1.96 Å), O(3)···O(6)' = 2.771(3) Å, O(4)···O(3)' = 2.701(3) Å and O(6)···O(2)' = 2.837(3) Å.

An analysis of the standard deviations in the C–C and C–O bond lengths as a function of a preset intensity threshold value has been carried out. Some results from this analysis are listed in Table 4 and shown in Fig. 3. We realize that the trend shown in Fig. 3 cannot be generalized, dut it is interesting to note that there in the present case is found to be an approximate linear relationship between the standard deviations and the threshold values for threshold values up to $10\sigma(I)$.

The changes in bond lengths as a result of the changes in intensity threshold value are all within one $\sigma$ and thus almost negligible, and the standard deviations in C–C and C–O bond lengths increase by a factor of only 1.5 for a change in intensity threshold value from $\sigma(I)$ to $10\sigma(I)$. The corresponding numbers of reflections per parameter are 13.8 and 4.3, respectively.

Similar analyses have been carried out for L,D-alanyl-D,L-methionine and *N*-acetyl-phenyl-alanyl-L-tyrosine by Stenkamp and Jensen.[14]

*Table 4.* Average values of standard deviations in C–C and C–O bond lengths, *R* factors, and numbers of observed ($N_o$) and unobserved ($N_u$) reflections from refinements with different intensity threshold values ($n\sigma(I)$). 157 parameters have been refined.

| | $\sigma(I)$ | $2\sigma(I)$ | $3\sigma(I)$ | $4\sigma(I)$ | $5\sigma(I)$ | $10\sigma(I)$ |
|---|---|---|---|---|---|---|
| $\bar{\sigma}(l)_{C-C}10^4$ Å | 26.4 | 28.6 | 30.0 | 31.8 | 33.8 | 41.0 |
| $\bar{\sigma}(l)_{C-O}10^4$ Å | 23.7 | 26.0 | 27.1 | 28.6 | 30.3 | 36.6 |
| $R$ | 0.078 | 0.061 | 0.047 | 0.040 | 0.036 | 0.026 |
| $N_o$ | 2174 | 1743 | 1405 | 1194 | 1038 | 672 |
| $N_u$ | 787 | 1218 | 1556 | 1767 | 1923 | 2289 |
| $N_o/157$ | 13.8 | 11.1 | 9.0 | 7.6 | 6.6 | 4.3 |

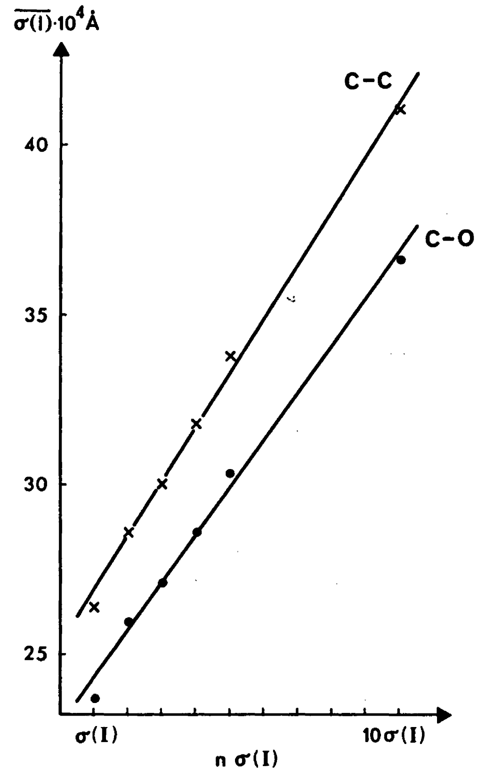


*Fig. 3.* The average standard deviations in C−C and C−O bond lengths in α-D-talose as a function of the intensity threshold value $n\sigma(I)$.

We have recently been informed that an independent structure study of α-D-talose has been carried out.[15] The results from the two studies are in excellent agreement.

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