# Crystal and Molecular Structure of D-*threo*-Hexo-2,5-diulose; Dimeric Form in the Solid State

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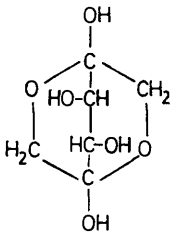
*Summary* In the crystalline state D-*threo*-hexo-2,5-diulose forms a dimer between a furanose form and a pyranose form of the sugar.

D-*threo*-HEXO-2,5-DIULOSE (**1**) is obtained as a metabolic product of acetic acid bacteria utilizing D-fructose or L-sorbose[1] and also as a bromine oxidation product of these sugars.[2] Molecular weight determination by a freezing point depression method shows that the compound occurs as a monomer in solution.[1] I.r. and n.m.r. spectra indicate that the sugar does not have free carbonyl groups, and the structure shown in Figure 1 (a) has been proposed as that most likely to be formed.[3] It contains two pyranose and one dioxan rings, all in the boat form.

The molecular structure of (**1**) has now been studied in the crystalline state by *X*-ray methods [see Figure 1 (b) and Figure 2]. It forms dimers which contain a furanose form as well as a pyranose form of the sugar, interconnected through C–O–C bonds. The bond lengths and angles are normal for such compounds.

(a)




(b)

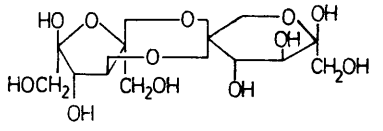



FIGURE 1. (a) Structure of D-*threo*-hexo-2,5-diulose previously proposed; (b) solid-state structure found in the present study.

TABLE. Atomic co-ordinates in fractions of corresponding cell edges with standard deviations in parentheses.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| O(1) | 0·2269(2) | 0·0830(1) | 0·4186(6) |
| O(2) | 0·3279(2) | 0·1070(1) | 0·8721(5) |
| O(3) | 0·4475(2) | −0·0025(1) | 0·9442(6) |
| O(4) | 0·6564(2) | 0·0456(1) | 1·0215(5) |
| O(5) | 0·6736(2) | 0·1766(1) | 0·9496(5) |
| O(6) | 0·4425(2) | 0·1346(1) | 0·5382(5) |
| O(11) | 0·7032(2) | 0·2933(1) | 0·7346(6) |
| O(12) | 0·8648(2) | 0·1623(1) | 0·9522(4) |
| O(13) | 0·6814(2) | 0·1144(1) | 0·6059(4) |
| O(14) | 0·9535(2) | 0·1711(1) | 0·4332(5) |
| O(15) | 0·8715(2) | 0·0552(1) | 0·8852(6) |
| O(16) | 1·0931(2) | 0·1667(1) | 0·8339(6) |
| C(1) | 0·3253(3) | 0·0503(2) | 0·4823(8) |
| C(2) | 0·3935(3) | 0·0850(2) | 0·6743(7) |
| C(3) | 0·4863(3) | 0·0447(2) | 0·7834(7) |
| C(4) | 0·5659(3) | 0·0821(2) | 0·9441(8) |
| C(5) | 0·6097(3) | 0·1361(2) | 0·7939(6) |
| C(6) | 0·5133(3) | 0·1725(2) | 0·6845(8) |
| C(11) | 0·7929(3) | 0·2597(2) | 0·8365(8) |
| C(12) | 0·7728(3) | 0·1905(1) | 0·8263(6) |
| C(13) | 0·7654(3) | 0·1591(1) | 0·5705(7) |
| C(14) | 0·8764(3) | 0·1276(2) | 0·5352(7) |
| C(15) | 0·9108(3) | 0·1135(2) | 0·8058(7) |
| C(16) | 1·0356(3) | 0·1100(2) | 0·8632(8) |

*Crystal data:* compound (**1**), $C_{12}H_{26}O_{12}$, colourless needles, elongated along *c*, orthorhombic, space group $P2_12_12_1$ with unit cell dimensions $a = 12{\cdot}094(3)$, $b = 21{\cdot}700(6)$, $c = 5{\cdot}329(3)$ Å. There are four dimer molecules per unit cell, $D_c = 1{\cdot}692$, $D_m = 1{\cdot}68$ g cm$^{-3}$.

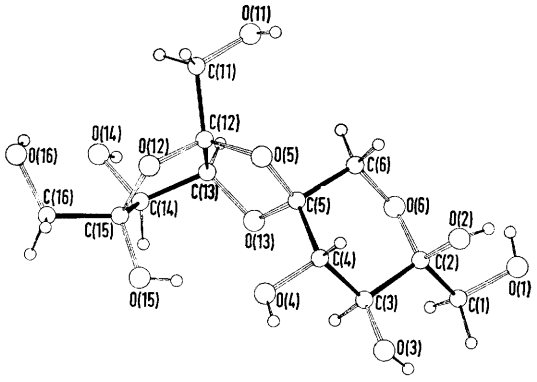



FIGURE 2. *X*-Ray structure of D-*threo*-hexo-2,5-diulose.

Using Mo-$K_\alpha$ radiation, 1443 out of 2174 independent reflections in the range $0 < \theta < 27°$ for which $I \geqslant 2\sigma(I)$ were accepted as observed. The structure was solved by direct methods (MULTAN)[4] and refined by full-matrix least squares. With anisotropic temperature coefficients for carbon and oxygen and isotropic for hydrogen the final *R* is 0·04.

The co-ordinates of the oxygen and carbon atoms are given in the Table.

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