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CRYSTAL STRUCTURE OF D-MANN-3-HEPTULOSE MONOHYDRATE

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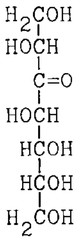
D-mann-3-heptulose (I) is one of the little known 3-heptuloses, and also coriose is. In the case of coriose, it has been shown that the molecule has a rather unexpected furanose structure in the crystalline state (1). In order to see if there is any similarity in the molecular structures of these two 3-heptuloses, an X-ray structure analysis was performed on the monohydrate crystal of (I).



$$\begin{array}{c} H_2COH \\ | \\ HOCH \\ | \\ C{=}O \\ | \\ HOCH \\ | \\ HCOH \\ | \\ HCOH \\ | \\ H_2COH \end{array}$$

(I)

The crystal data are; formula, $C_7H_{14}O_7 \cdot H_2O$; orthorhombic, space group, $P2_12_12_1$, Z=4; cell dimensions, a=17.80±0.02 Å, b= 7.356±0.005 Å, c=7.349±0.005 Å; density, D_o=1.577±0.003 g.cm.$^{-3}$, D_c=1.575±0.005 g.cm.$^{-3}$. Intensities of 1257 independent reflections were visually estimated from the Weissenberg photographs about b- and c-axes recorded with Cu Kα radiation. They were reduced to absolute scale by the Wilson's method and normalized structure factors |E| were obtained.

The structure was determined by the application of a symbolic addition procedure for noncentrosymmetric crystal (2). The approximate positions of all the carbon and oxygen atoms were revealed from the E-map computed with 145 phases, which had been determined by this procedure. R-factor for this structure was 0.44 for the reflections with $\sin\theta < 0.8$. After the positions of three atoms C_1, O_1 and O_8 were corrected by Fourier synthesis, four cycles of diagonal least squares refinements reduced the R-factor to 0.15. The positions of hydrogen atoms were assumed referring to the difference Fourier map and were included in the subsequent structure factor calculations. Further three cycles of least squares refinements reduced the R-factor to 0.10 for all the reflections. The final atomic positions and isotropic temperature factors are listed in Table 1.

The molecule was found to have β-pyranose configuration given in Fig.1. The six-membered ring has the chair form. O_3 and O_6 are in axial and O_4 and O_5 are in equatorial positions. The covalent bond distances and angles are shown in Fig.1 and Fig.2. The mean values of C-C and C-OH distances are 1.535 Å and 1.439 Å, respectively. C_3-O_3 distance of 1.418 Å is significantly shorter than the normal value 1.43 Å.

The crystal structure is composed of the three dimensional network of hydrogen bonding. The water molecule is hydrogen-bonded to three different sugar molecules and takes part in this network.

The FORTRAN programs used for all the computations were prepared by T.Taga.

We wish to thank Dr. Takuo Okuda of the same Faculty for suggesting the problem and supplying us with suitable crystals. We also thank the Kyoto University Computation Center for computing facilities.

Table 1

	x/a	y/b	z/c	B
C_1	0.1260	0.4675	0.4059	2.65
C_2	0.0739	0.6276	0.3645	1.66
C_3	0.0749	0.7734	0.5125	1.19
C_4	0.1475	0.8881	0.5209	1.40
C_5	0.1437	1.0152	0.6824	1.29
C_6	0.1313	0.9064	0.8604	1.80
C_7	0.0572	0.7979	0.8370	2.06
O_1	0.1245	0.3500	0.2509	2.42
O_2	-0.0025	0.5678	0.3536	2.25
O_3	0.0134	0.8922	0.4829	1.80
O_4	0.1536	0.9911	0.3546	1.52
O_5	0.2144	1.1146	0.6915	1.88
O_6	0.1925	0.7811	0.8880	2.33
O_7	0.0646	0.6797	0.6798	1.55
O_8	0.1809	0.3978	0.9030	3.49

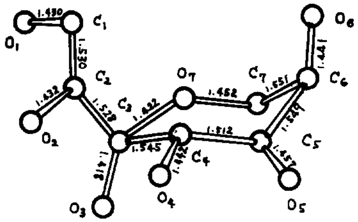


Fig. 1 (Å)

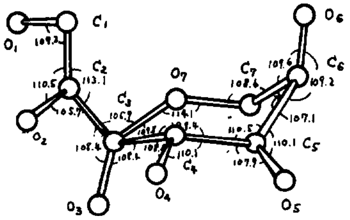


Fig. 2 (degree)

(1) T.Okuda, K.Osaki & T.Taga, Chem. Comm. (1969) (in press).

(2) J.Karle & I.L.Karle, Acta Cryst., 21, 849, (1966).