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CRYSTAL STRUCTURE OF A β-CYCLODEXTRIN·ETHANOL·OCTAHYDRATE

Ryoji TOKUOKA, Masako ABE, Takaji FUJIWARA,
Ken-ichi TOMITA, and Wolfram SAENGER*
Faculty of Pharmaceutical Sciences, Osaka University
133-1, Yamada-kami, Suita, Osaka 565
*Abteilung Chemie, Max-Planck-Institut für experimentelle
Medizin, Hermann-Rein-Strasse 3, D-3400 Göttingen(Germany)

Ring-shaped β-cyclodextrin(β-CD) molecules as hosts enclosing ethanol and three water molecules as guests are arranged in cage-type structure produced by the twofold screw axis of the monoclinic crystal system; space group $P2_1$, a=21.115, b=10.190, c=15.214Å, β=111.4°, Z=2. Between the β-CD, five waters are located. Each of the guest ethanol, two waters and three primary hydroxyls are distributed at two alternative sites. The possibility of a structural transition from cage to channel type is considered.

β-CD is a cyclic heptasaccharide consisting of α-1,4-linked glucose units. As a host, it forms inclusion compounds with various guest molecules. We were interested to see in which type(cage or channel) of crystal packing the complexes with ethanol would arrange because both β-CD·water[1] and β-CD·methanol[2] crystallize in a cage type structure whereas the higher homologue of ethanol, in the β-CD·n-propanol complex[3], forms a channel. We describe here briefly the X-ray crystal and molecular structure of the β-CD·ethanol inclusion compound.

Crystals of this complex were obtained by dissolving β-CD in hot,65% aqueous ethanol and by slow cooling of the samples in a Dewar flask filled with hot water. The crystal density(D_m=1.443 Mg/m^3) and the unit cell volume indicate that an asymmetric unit contains β-CD·ethanol·octahydrate. A crystal of dimensions 0.15x0.20x 0.35 mm3 sealed in a Lindemann glass capillary with some mother liquid was used for the collection of 3585 independent non-zero X-ray data with a Rigaku Denki four-circle automatic diffractometer. The crystal structure was solved by application of the crystallographic data of an isomorphous derivative, β-CD·methanol heptahydrate[2]. The refinements by successive Fourier, difference Fourier syntheses and a full matrix least-squares procedure[4] applying constraints to bond distances and angles of the β-CD moiety, dropped the R to 11.7% for the strongest 2000 reflections. Further refinements by the conventional block diagonal least-squares program[5] with anisotropic temperature factors for non-hydrogen atoms converged the R to 11.5% for all 3585 reflections.

The overall structure of the host β-CD molecule in this complex is very similar to the one in complexes with dodecahydrate[1] and with methanol heptahydrate[2].

Bond lengths and angles within the β-CD molecule are normal. All the glucose units are in a C1 chair conformation and the intramolecular O(2)···O(3) hydrogen bonds between the neighbouring glucose units fix the β-CD molecule to an almost round shape. Seven glucoside oxygen atoms (O4 in Fig.1) form a plane with a maximum atomic deviation of 0.32 Å. The dihedral angles between this plane and a plane defined by C2, C3, O5 and C5 atoms were calculated for all glucose units in order to present the β-CD ring conformation. They range from 69° to 86° as shown in parentheses in Fig.1, and the glucose units I, II, IV and V are tilted more than the others. It is interesting to note that three disordered O6 atoms belong to the glucose units I, II and IV, as indicated by dotted lines in Fig.1. The disordered orientations of C6-O6 bonds with respect to the C5-O5 bonds are found to be (-)*gauche*, whereas the ordered one adopt the preferred (+)*gauche* conformation. Three water molecules (W5, W6 and W8) and one ethanol molecule are included within the β-CD cavity, in which one water molecule (W5) and the ethanol molecule are disordered. As shown schematically in Fig.2, the disordered ethanol molecules (EtOH1 and EtOH2) can not be accommodated simultaneously within the cavity. The oxygen atom of EtOH1 occupies the position near the secondary hydroxyls (the wide side of the cavity) and is connected with two adjacent β-CD molecules by three hydrogen bonds. On the other hand, the EtOH2 molecule is in the opposite direction, and its oxygen atom points towards the primary hydroxyls (the narrow side of the cavity) and forms two hydrogen bonds with water molecule (W6) and the primary hydroxyl oxygen atom (O6). Ethyl groups of both ethanol molecules contact with the inner surface of the cavity with normal van der Waals distances.

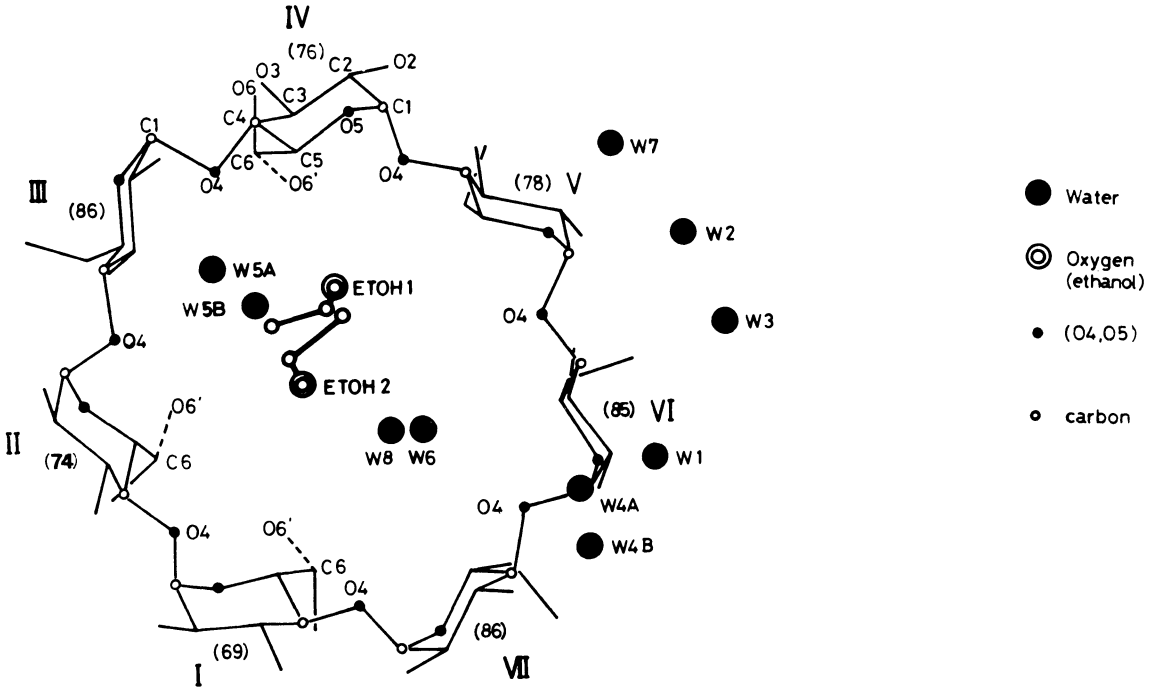

Fig.1. Structure of β-CD ethanol octahydrate, projected on the O(4) least-squares plane. Dihedral angles(°) between the O(4) plane and planes defined by C(2), C(3), O(5) and C(5) atoms, are shown in parentheses.

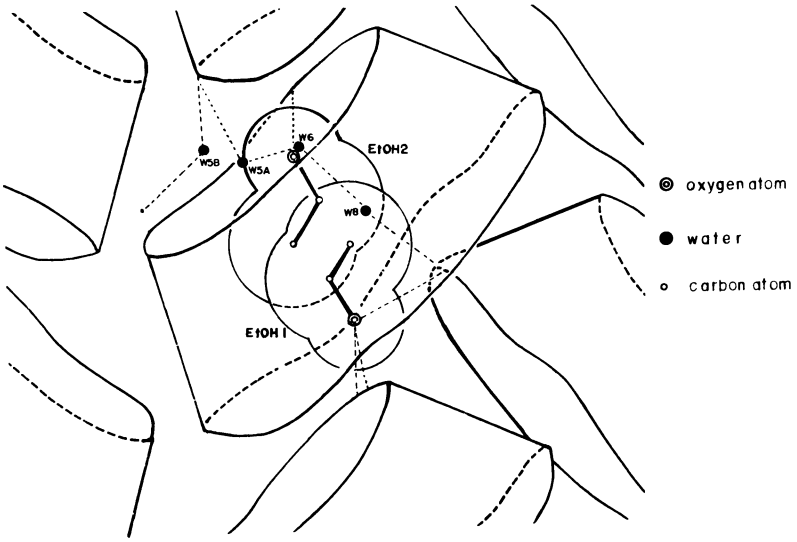

Fig. 2. Schematic drawing of included ethanol and water molecules within the β-CD cavity.

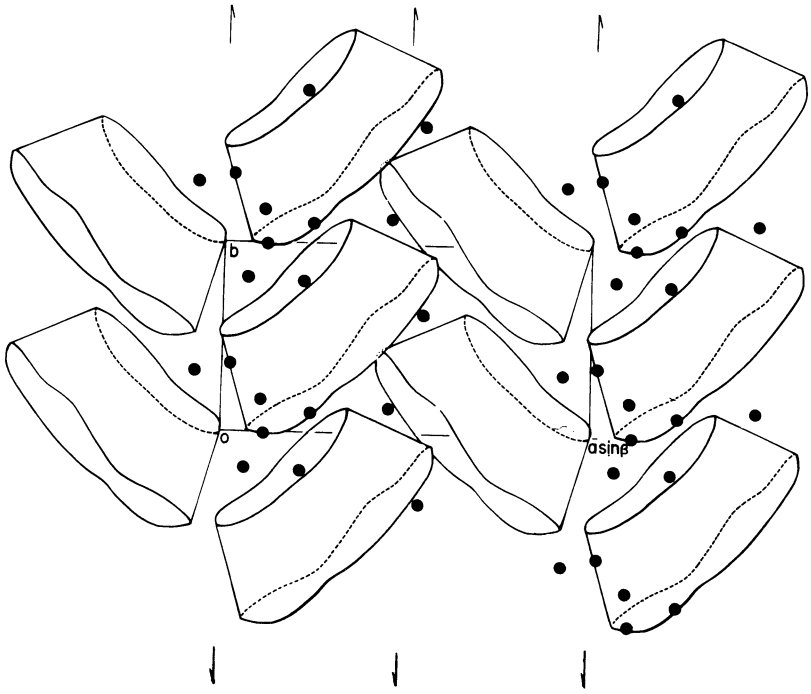

Fig. 3. c-axis projection of the crystal structure of β-CD ethanol octahydrate. β-CD molecules are drawn schematically.

Five water molecules involving a disordered W4 are located outside the cavity and appear to play an important role in stabilizing the crystal structure by a network of hydrogen bonds. As shown in Fig.3, there are two different crystal packings along twofold screw axes at x=0 and (x=1/2,z=1/2): around the twofold screw axis at x=0, there is only little contact between β-CD molecules and many water molecules occupy a vacant space, whereas around the other axis β-CD molecules are tightly packed with only a few water molecules between them.

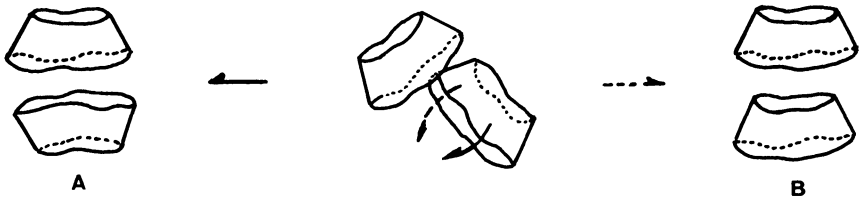

Fig.4. Schematic representation of two possible β-CD packings (head-to-head (A) or head-to-tail (B)) as a basic unit for channel type packing from the cage type packing of β-CD ethanol complex.

Fig.4 demonstrates a possibility of forming channel type packings from the cage type structure found around the twofold axis at (x=1/2,z=1/2). The channel structures are stabilized by hydrogen bonds between primary/secondary hydroxyl group. The head-to-tail form has not been observed thus far but the head-to-head structure has been found in complexes of β-CD with n-propanol[3], 2,5-diiodobenzoic acid[6] and p-nitroacetanilide[7].

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