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Structure of 6-O-α-D-Glucopyranosyl α-Cyclodextrin•$8H_2O$

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Cryatal and molecular structure of a branched α-cyclodextrin, 6-O-α-D-grucopyranosyl α-cyclodextrin was studied by X-ray structure analysis. A branched grucopyranose moiety is included in the cavity of another α-cyclodextrin moiety from the side of its secondary hydroxyl groups.

6-O-α-D-glucopyranosyl α-cyclodextrin (G_1-α-CyD) is a branched α-cyclodextrin (α-CyD), that is composed of α-CyD moiety and one glucopyranose residue attaching to one of α-CyD constituents through α(1-6) glucosidic linkage as shown in Fig. 1. G_1-α-CyD is produced as a component via a limited action of Bacillus macerance glucanotransferase on waxy corn starch, and can be isolated from the other sugar derivatives by the procedures of Kobayashi et al.[1-2] Due to this branch, G_1-α-CyD is more water-soluble and more resistant to enzymic degradation than the parent α-CyD, and structure determination of G_1-α-CyD is very important to better understanding for the basic structure of starch and action of glucanotransferase.

We report here briefly the crystal and molecular structure of G_1-α-CyD•$8H_2O$.

G_1-α-CyD•$8H_2O$ was crystallized as follows; one gram of pure G_1-α-CyD (purity: more than 99.8%) was dissolved in 1ml of water by standing in a boiling water bath, and the solution was gradually cooled (for 6 h at 70 °C, for 6 h at 50 °C, overnight at 25 °C, for a week at 4 °C). The mother liquor was transferred to a new 5 ml vial, 1-2 fine crystals were placed in it and the vial was stored with the lid open in a dust free cold room at 4 °C for 1-2 month to elongate the crystals.

A transparent colorless crystal of 0.30x0.35x0.60 mm^3 size was used for the

X-ray diffraction measurements. The crystal data are : $C_{42}H_{70}O_{35}\cdot 8H_2O$, F.W.= 1279.1, Orthorhombic, $P2_12_12_1$, Z=4, a=21.818(1), b=19.310(1), c=13.507(1)Å, V=5690.7(5)Å^3, F(000)=2728, Dx=1.493 Mg m^{-3}, μ(Cu-Kα)=11.99 cm^{-1}. The intensities of 4874 reflections were obtained at 293 K using Rigaku Automatic four circle diffractometer(AFC-5) with Cu-Kα radiation(λ=1.5418Å) and ω-2θ scan with a $2\theta < 125°$.

The structure was solved by the direct method SIR85.[3] The refinements was carried out by the block-diagonal least-squares method with anisotropic temperature factors and a unit weight for all reflections. Almost all hydrogen atoms were assigned on a difference Fourier map and were included in the refinement with isotropic temperature factors. The final R value was converged to 0.051 for 4874 reflections with $|F_o| > 3\sigma(|F_o|)$. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[4]

All computations were carried out with the IBM 3081-GX3 computer at Information Processing Center, Shimane University.

As shown in Fig. 1,[5] overall shape of the α-CyD moiety is round, however, owing to the O6---W2 hydrogen bond of 2.866(13)Å the glucopyranose unit 2 (G2) inclines so greatly as the O6 atom coming near to a center of the α-CyD cavity, and the six glucoside atoms (O4) are not in a plane (max. deviation of 0.350(4)Å from the least-squares plane is lager than 0.135(6)Å of α-CyD·6H$_2$O[6] and 0.148(6)Å

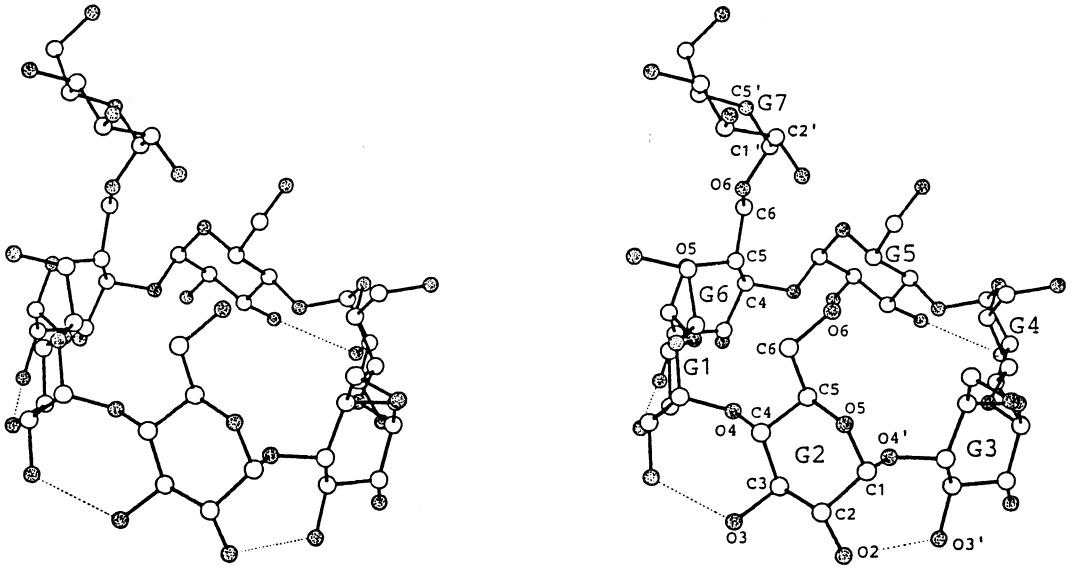

Fig. 1. Structure of the branched α-cyclodextrin. Glucopyranose unit n are numbered as Gn. Oxygen atoms are shown by the dotted circles. Hydrogen bonds are indicated by broken lines.

of α-CyD·7.57H_2O[7]). The intramolecular hydrogen bonds of O2---O3' are in G1-G2, G2-G3, G4-G5, and G6-G1, but not in G3-G4, and G5-G6. The conformations about the C5-C6 bond, C4-C5-C6-O6 and O5-C5-C6-O6, for G1, G3, G4, G5, and G7 units are both gauche, that is, the C6-O6 bonds direct outside to the α-CyD ring. On the other hand, those for G2 and G6 are trans and gauche respectively, the C6-O6 bond lies parallel to the α-CyD ring. About the α(1-6) glucosidic linkage between G6 and G7, the conformation of C5-C6-O6-C1' is trans, and the conformations of C6-O6-C1' -C2' and C6-O6-C1'-O5' are trans and gauche respectively. The G7 unit extends parallel to the α-CyD wall like 'just open a can'.

As shown in Fig. 2,[8] a branched glucopyranose moiety is included deeply into the cavity of another G_1-α-CyD from its O2, O3 side. Both G_1-α-CyDs are related by two-fold screw axis. The dihedral angle between the two planes through six O4 atoms of each α-CyD moiety is 121°. Two G_1-α-CyDs are arranged in head to tail fashion like a symbol of <, resulting in a zigzag chain along the b-axis. The two chains running in opposite directions to each other construct the crystal structure as shown in Fig. 3.

There are eight crystalline waters per one G_1-α-CyD. These waters play an important role to built up the crystal structure by hydrogen bonding. Two waters, W1 and W2 are in the α-CyD cavity, other six waters are out of it. W1 connects

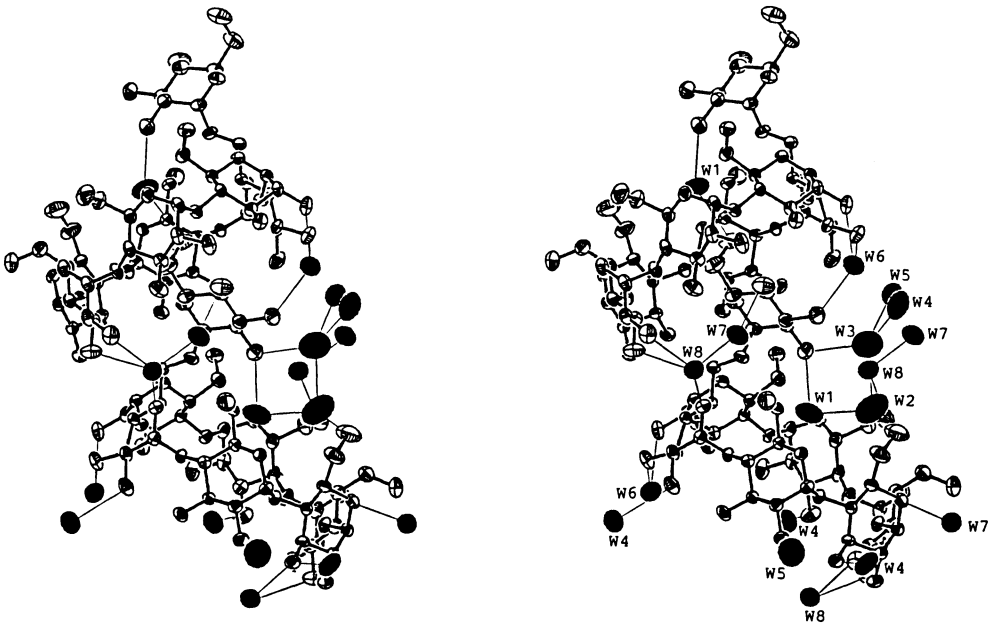

Fig. 2. Stereoscopic view for two units of the branched α-cyclodextrin. The hydrogen bond is indicated by a thin line. Water molecules are represented by solid circles.

two G_1-α-CyDs by O6(G7)--W1--O2(G7') hydrogen bond of 2.775(11)Å, 2.764(10)Å through α-CyD cavity. W1 to W5 make a water-cluster, while W7 and W8 make another one. The waters connect secondary (O2, O3) and/or primary (O6) oxygen atoms by intermolecular hydrogen bonding including -W---W- type of hydrogen bond. The crystal structure is also stabilized by direct hydrogen bonding at O2, O3 and O6 atoms of the neighbouring α-CyDs, as shown in Fig. 3.

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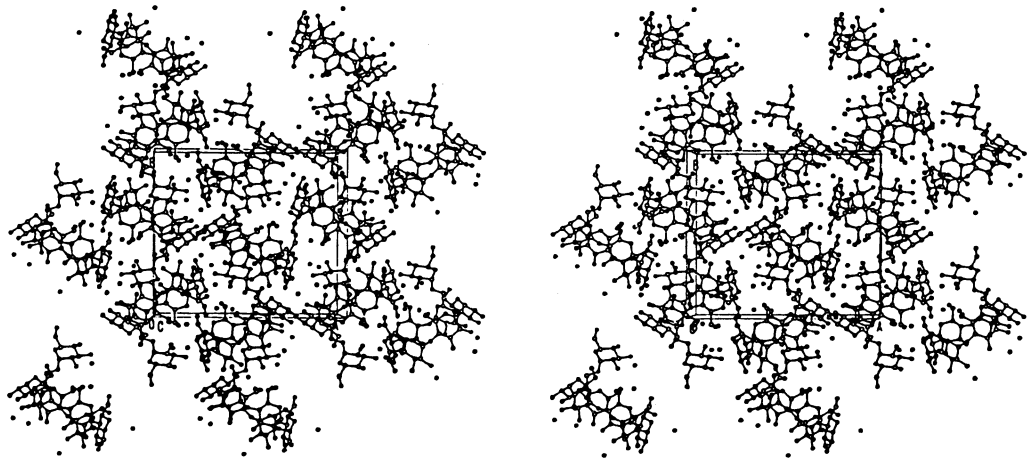

Fig. 3. Crystal structure of 6-O-α-D-glucopyranosyl α-cyclodextrin•$8H_2O$.

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