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Crystal Structure of Cycloinulohexaose

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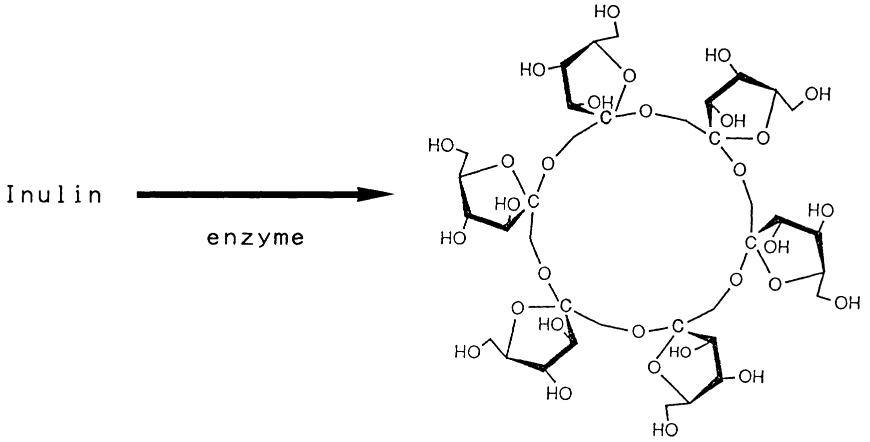
X-Ray crystallography analyzed cycloinulohexaose, $C_{36}H_{60}O_{30}$, whose 18-crown-6 skeleton was the GTGTGT conformational arrangement of the six sequential $-O-C-CH_2-O-$ units.

The cycloinulohexaose ($C_{36}H_{60}O_{30}$) was produced from inulin by an extracellular enzyme [cycloinulo-oligosaccharide fructanotransferase] of Bacillus circulans OKUMZ31B. The cyclofructan is a β-(2→1) linked cyclohexaose of D-fructofuranose. The chemical structure has been determined by means of enzymic, spectroscopic, and chromatographic analyses.[1] We have been strongly interested in the macrocyclic conformation of this type of molecules, because it has the characteristic 18-crown-6 skeleton.



We now communicate here the crystal structure of the cycloinulohexaose which is the main product of cycloinulo-oligosaccharide fructanotransferase reaction.

The crystal data are as follows: $C_{36}H_{60}O_{30}\cdot 3H_2O$, M=1026.9, trigonal, space group R3 (hexagonal axes), a=b=24.688(17), c=6.477(3) Å, $\alpha=\beta=90.00^{\circ}$, $\gamma=120.00^{\circ}$, V=3419(4) $Å^3$, Z=3 molecules/cell, $D_c=1.50$ $g\cdot cm^{-3}$. Reflections of 4871 with $2\theta\leq 55^{\circ}$ were recorded on a Rigaku AFC-5FOS four-circle diffractometer by using graphite-monochromated Mo-Kα radiation. Of these 1698 (with $F_o>3\sigma(F)$) were used for solution. One third of the molecule (inulobiosyl unit; $C_{12}H_{20}O_{10}\cdot H_2O$) could be solved by means of MULTAN78.[2] Block-diagonal least squares refinement with anisotropic temperature factors for non-hydrogen atoms converged successfully to R=0.059; eighteen hydrogen atoms out of twenty two were located through difference synthesis.

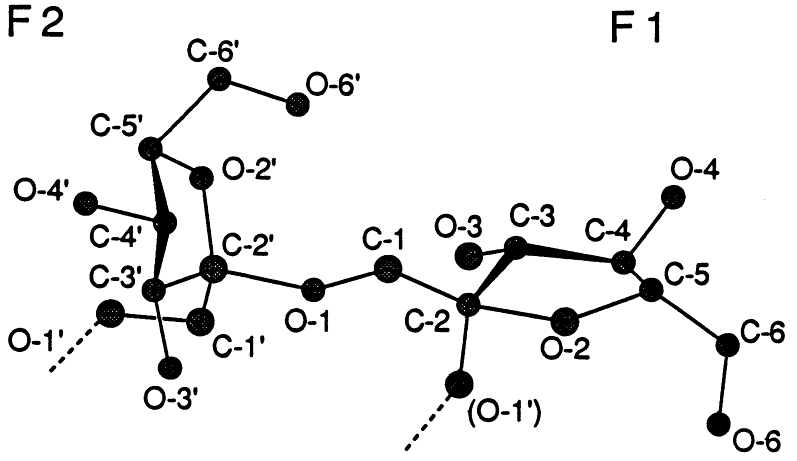


Fig. 1. A perspective view of the inulobiosyl unit with numbering.

The fructofuranosyl moieties in inulobiosyl unit (1-O-β-D-fructofuranosyl β-D-fructofuranose) have almost the same conformations with the exception of the torsion angles, O-1-C-1-C-2-C-3, of -71.7° and $+45.9^{\circ}$ in F1 and F2, respectively. Both puckerings of the furanose rings of F1 and F2 are $^4T_3$ (Fig. 1).[3,4]

Figure 2 is ORTEP drawings of the cycloinulohexaose. For the moiety of the 18-crown-6 skeleton, the torsion angle of O-1-C-1-C-2-O-1' in F1 is $+52.3^{\circ}$, and that of the corresponding O-1'-C-1'-C-2'-O-1 in F2 is $+163.4^{\circ}$: deviations out of the ideal gauche (G) and trans (T) positions are 8° and 17°, respectively. Therefore, the cycloinulohexaose molecule has the GTGTGT conformational arrangement of the six sequential $-O-C-CH_2-O-$ units.

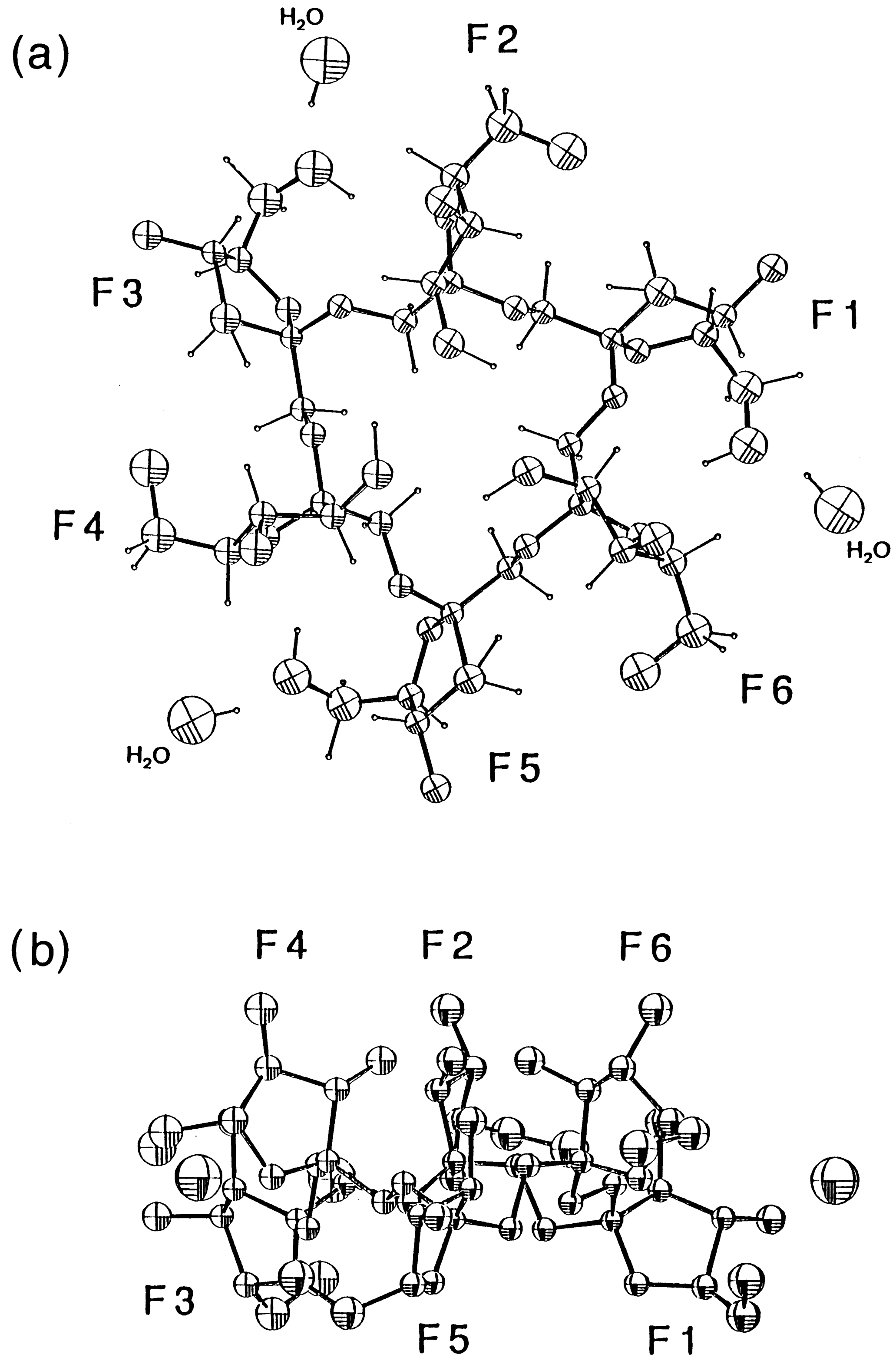


Fig. 2. ORTEP drawings of cycloinulohexaose. (a) a top view (H atoms solved are included); (b) a side view (H atoms are excluded).

This type of arrangement is completely different from the GTGGTG observed for the case of uncomplexed 18-crown-6,5, 6) and the GGGGGG observed for the case of K^+ ion-complexed 18-crown-6.7, 8)

It should be noted that the oxygen atoms (O-3') bonded to C-3' in **F2**, **F4**, and **F6** are very close to each other. The distance between the oxygens is 3.09 A, which is approxymately the sum of van der Waals radius of two oxygens. Accordingly, the one side of the 18-crown-6 ring is covered by these three oxygens. The other side of the ring is exolipophilic mainly due to the existence of the carbon groups in gauche -O-C-CH_2-O- unit. The potentially polarophilic crown-ring oxygens9, 10) are then almost folded inside in this molecule.

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