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Inter-chain and arrayed hydrogen bonds in β-1,3-D-xylan triple helix predicted by quantum mechanics calculation

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Abstract

β-1,3-D-xylan and β-1,3-D-glucans take the similar 6-hold right-handed triple helix. According to the classical model, three second hydroxyl groups form a hexagonal shape inter-chain hydrogen bond. Recent progress in computational chemistry proposed two other possibilities for the hydrogen bonds. Both models proposed formation of a hydrogen-bond array along the helix. The difference between them is that: one is an intra-chain and the other is an inter-chain. We compared these three models with MOPAC and B3LYP methods and concluded that the inter-chain and arrayed hydrogen bond is the most realistic one.

Keywords: β-1,3-D-xylan; Curdlan; Hydrogen bond; Triple helix; β-1,3-D-glucan; MOPAC calculation; B3LYP method

1. Introduction

Certain plants in siphoneous green algae contain a polysaccharide called β-1,3-D-xylan (Fig. 1) in the cell wall (Atkins & Parker, 1968, 1969; Rao, Qasaba, Balaji, & Chandrasekaran, 1998). X-ray crystallography showed that β-1,3-D-xylan adopts a 6-fold right-handed triple helix. The pitch varies according to humidity: it is 18.36 Å in the wet state and 17.55 Å in the dry state. The crystallographic group of β-1,3-D-xylan is categorized to a hexagonal system, and the dimensions of the unit cell are $a = b = 15.4$ Å and c (fiber axis) $= 6.12$ Å in the wet state, and $a = b = 13.7$ Å and $c = 5.85$ Å in the dry state (Atkins & Parker, 1969). Type A in Fig. 2 shows the molecular model established by Atkins et al., as well as the hydrogen bonds that connect the three xylan chains. Since the first structural analysis, it has been widely accepted that a hexagonally shaped hydrogen bond is formed at the center of the helix as presented in the panels Fig. 2(b). Here, three second hydroxyl groups form three inter-chain hydrogen bonds and the direction of the hydrogen bonds is perpendicular to the helix axis.

The structural features of β-1,3-D-xylan helix are almost the same as those of β-1,3-D-glucans (eg., curdlan and schizophyllan) because of similarity in the chemical structures. In fact, the crystal structure of curdlan and schizophyllan is close to that of β-1,3-D-xylan (Atkins & Parker, 1969) and thus it has been considered that curdlan and schizophyllan take a hexagonally shaped hydrogen bond similar to Type A in Fig. 2. In 2000, Frecer et al. (Frecer, Rizzo, & Miertus, 2000) studied the conformations of β-1,3-D-glucans by means of molecular mechanics and molecular dynamics simulations and pointed out the possibility that an intra-chain hydrogen bond can be formed between adjacent second hydroxyl groups. Recently, we carefully re-examined the positions of the hydrogen atoms in the curdlan triple helix by use of a semi-empirical quantum mechanics (MOPAC) and proposed another model for the hydrogen bond (Deslandes, Marchessault, & Sarko, 1980; Miyoshi, Uezu, Sakurai, & Shinkai, 2004). Although

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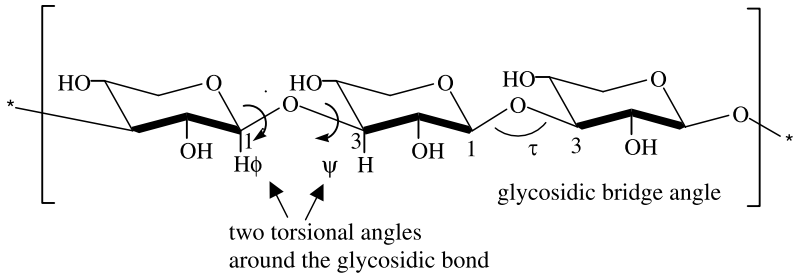

Three key parameters (ϕ,ψ , τ) of curdlan and β-1,3-D-xylan

	ϕ	ψ	τ
curdlan	29.1°	9.6°	110.4°
xylan	26.8°	4.8°	106.3°

Fig. 1. Repeating unit of β-1,3-D-xylan and the definitions of the two torsional and bridge angle to determine the conformation. The inset table compares the three angles between β-1,3-D-xylan and curdlan.

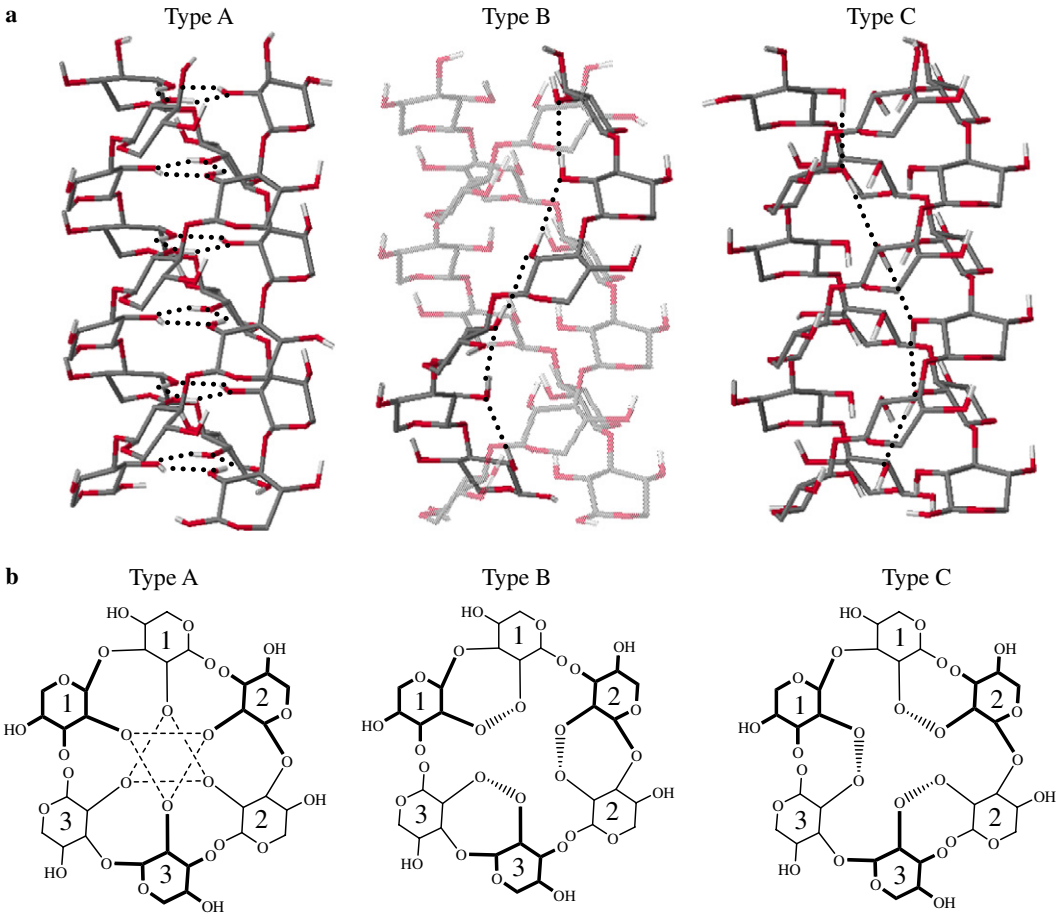

Fig. 2. Molecular models of Types A, B, and C. (a) The side view of the triple helix, here the dot-lines indicate the hydrogen bonds. (b) The top view of the helix. Two xyloses of each chain. The same number indicates the same chain and the bold lines present the xyloses in the front. In Type A, a hexagonal hydrogen bond is formed between three xyloses. In Type B, an arrayed hydrogen bond is formed within the same chain. In Type C, an arrayed hydrogen bond is formed between three chains.

these models are proposed for β-1,3-D-glucans, the same discussion can be made on β-1,3-D-xylan. In Fig. 2, Types B and C present the hydrogen bonds for β-1,3-D-xylan, corresponding to Frecer's and our models, respectively. In the Frecer's model, a hydrogen-bond array is formed to connect the second hydroxyl groups on the same curdlan chains (intra-chain) and thus the hydrogen-bond array makes the same right-handed helix as the main chain. On the other hand, a left-handed helix (reverse to the main chain) is formed in our model because the hydrogen bonds between the second hydroxyl groups connect the different chains (inter-chain). By MOPAC calculations, it was found that our Type C model is the most stable form among three types. The formation of long hydrogen-bond array is a common feature between Frecer's Type B and our Type C models and a distinctive difference from the original Atkins Type A model. Free energy calculation showed that the hydrogen-bond array becomes more stable in the longer chains owing to the delocalization of the electrons that consist of the hydrogen bonds (Miyoshi et al., 2004). As a result, the Type C was more stable than the Type A in curdlan structure. The knowledge of hydrogen-bonding type is very important, because the difference of hydrogen-bonding type can affect a molecular property. Thus, it is necessary to determine if the Type C is also a stable form on β-1,3-D-xylan triple helix in which the Type A was first proposed.

This paper re-examines β-1,3-D-xylan by means of computational chemistry. Although the xylan structure is similar to that in curdlan, the absence of the 6-hydroxyl groups in xylan may differentiate the triple helix. In this study, we explore the hydrogen bonds in the β-1,3-D-xylan triple helix by MOPAC and B3LYP methods, and compare with curdlan.

2. Experimental

2.1. Construction of the β-1,3-D-xylan structure

Since the xylose ring takes the chair conformation at moderate temperatures, two torsional and one bridge angles around the glycosidic bond essentially determine the entire conformation of the polysaccharide (Rao et al., 1998). These key parameters are defined by ϕ(H1–C1–O3′–C3′), ψ(C1–O3′–C3′–H3′), and τ(C1–O3′–C3′) as illustrated in Fig. 1. According to the crystallographic data determined by Atkins and Parker (1969), $\phi = 26.8$, $\psi = 4.3°$ and $\tau = 106.3°$ for β-1,3-D-xylan (the inset table compares the parameters between xylan and curdlan). Since we are only interested in the hydrogen bonds in the xylan, we used these values. We constructed the xylan that consists of 36 xylose units and 621 atoms in total corresponding to 2 pitches of the helix. The positions of hydroxyl hydrogen atoms are not provided by X-ray diffraction. As the initial calculation condition, we attached all hydroxyl hydrogen atoms to the sp^3 orbital of the oxygen. For the hydroxyl hydrogen, the bending angle of C–O–H was set at 109.5° and the torsional angle around C–O was allowed to rotate freely.

2.2. Calculation

We fixed the coordinates of the oxygen, carbon and methylene hydrogen atoms in the β-1,3-D-xylan at the position determined by X-ray, as mentioned above, and the second hydrogen atoms are located to take one of the three types in Fig. 2. The coordinates of other hydroxyl hydrogen atoms were determined by the geometry optimization of MOPAC. These three sets of the coordinates are the initial conditions of the calculation. The calculations were carried out using MOPAC2002 (Stewart, 1990) in CAChe 5.0 version (Fujitsu Ltd., Japan). In this work, all calculation was done in vacuum mode and AM1 method was employed because of accuracy to describe hydrogen bonds (Dewar, Xoebisch, Healy, & Stewart, 1985). For the other parameters, the default values in MOPAC were used. MOPAC calculates the wave functions for all atoms based on a semi-empirical Hamiltonian and evaluates the heat of formation (HOF) (Stewart, 1990).

Since MOPAC may have ambiguity owing to the semi-empirical approximation, we confirmed the MOPAC result by use of a Gaussian calculation. A single-point energy calculation of the 12 xylose units models was conducted by the three-parameter hybrid Hatree-Fock/density functional (B3LYP) method in the Gaussian 03 program package (Frisch et al., 2003). The 6-31G* basis set was employed for all atoms. In the Gaussian calculation, we had to use a shorter chain than that of MOPAC calculation because of the limitation of our computer power.

3. Results and discussion

3.1. Conversion of the hydrogen-bond type after MOPAC calculation

Table 1 summarizes the results of the MOPAC calculation, comparing with those of curdlan (Miyoshi et al., 2004). When we started the optimization from Type A, it always converted to Type C, similarly to curdlan. When we started from Type C, it stayed at Type C and never changed to the other types, again, similarly to curdlan. On the other hand, when we started from Type B, the final structure never fit into any type in Fig. 2, while, in the case of curdlan, Type B stayed at Type B. The calculated HOF shows that the new type (denoted by RC) is more stable than that of Type C.

To confirm the HOF difference between RC and C types, we compared the HOF values obtained by the B3LYP method. The result showed that Type RC was more stable than Type C by 18 kcal/mol, agreeing with the MOPAC results (see Table 2).

Type A did not convert to Type RC although Type RC was the most stable form. This is because there is a large potential barrier between Type A and Type RC, and thus

Table 1
Heat of formation and H-bond type in the xylan and curdlan models obtained by MOPAC calculation

Model	H-bond type before	H-bond type after calculation	Heat of formation (kcal/mol)
Xylan A	A	C	−3357
Xylan B	B	RC	−3386
Xylan C	C	C	−3358
Curdlan A	A	C	−7517
Curdlan B	B	B	−7505
Curdlan C	C	C	−7518

A, Intermolecular O2–O2H (triangle); B, intramolecular O2–O2′H (right-handed helix); C, intermolecular O2H–O2′ (left-handed helix); RC, Intermolecular O2–O2′H (left-handed helix).

Table 2
Absolute energies obtained by B3LYP calculations

H-bond type	Absolute energy (kcal/mol)
C	−3879597
RC	−3879615

the iteration of MOPAC did not overcome this barrier. MOPAC calculations provide the most stable atomic coordinates at the absolutely zero temperature and do not take into account thermal fluctuation. Therefore, at ambient temperatures, the conversion from Type C to RC or a mixed state of both would be more likely. The most important conclusion in this calculation is that Types A and B are not produced by MOPAC calculation.

3.2. Comparison between Types RC and C

Fig. 3(a) shows the structural difference between Types C and RC. In Type C, H2 of the strand 2 forms the hydrogen bond with O2 of the strand 3, as a result, it turns down to the direction of the reducing end. On the other hand, in Type RC, H2 forms the hydrogen bond with O2 of the strand 1 and it turns up to the opposite direction of the reducing end. In both types, the hydrogen bond is formed between the adjacent O2 on the different chain, and the left-handed helical hydrogen-bond array is created. The difference between Types C and RC is the direction of H2 atoms, in another word, which oxygen atom mainly occupies H2. Table 3 compares the averaged O–H bond orders between Type C and Type RC. The hydrogen-bond order of Type RC is larger than that of Type C, indicating that the H2 proton in Type RC is more shared owing to the hydrogen bond than that of Type C. This is the reason that HOF of Type RC is smaller than that of Type C.

Proton-transfer between two O2 atoms makes the difference indistinct between Types C and RC. In fact, there should be no practical difference between them at ambient temperature. Both Types C and RC can be categorized into an inter-chain and hydrogen-bond array type. On the other hand, Type A is an inter-chain and discontinuous hydrogen-bond type and Type B is an intra-chain and hydrogen-bond array type. Therefore, the major conclusion in our calculation is that the inter-chain and hydrogen-bond array type is the most realistic model for β-1,3-D-xylan.

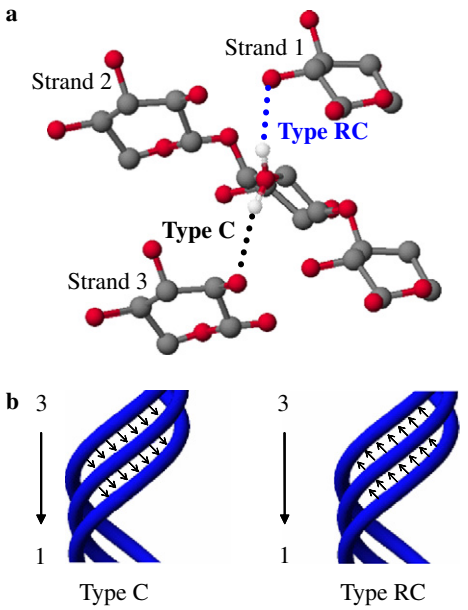

Fig. 3. Structure differences between Types C and RC. In Type C, H2 forms the hydrogen bond with O2 of the strand 3 and turns down to the direction of the reducing end. In Type RC, H2 turns up to form the hydrogen bond with O2.

Table 3
Comparison of the bond order between Types C and RC

	Between O2 in Strand 1 and H2 in Strand 2	Between O2 in Strand 3 and H2 in Strand 2
Type C	H-bond 0.00108	Non-bonding 0
Type RC	Non-bonding 0	H-bond 0.00115

Our pervious paper clarified that the longer hydrogen-bond array gives the less HOF, supporting that the stabilization of the array can be provided by the hydrogen-bond cooperativity that induce the delocalization energy. This length effect is consistent with the experimental results that the triple helix formation occurs when the number of glucose exceeds about 15. When the single chains of curdlan (also β-1,3-D-xylan) are re-natured in appropriate conditions, triple helix is re-formed. This fact is consistent with that the inter-chain hydrogen bond is more favorable than the intra-chain one. These two features (length effect and inter-chain hydrogen bond) agree with our conclusion that the inter-chain and hydrogen-bond array type is the most realistic model.

3.3. Conformational difference between xylan and curdlan

According to the crystallographic results (Atkins & Parker, 1969; Deslandes et al., 1980), there is a slight difference in the atomic coordinates between β-1,3-D-xylan and curdlan as presented in Fig. 4. As presented in Fig. 4(a),

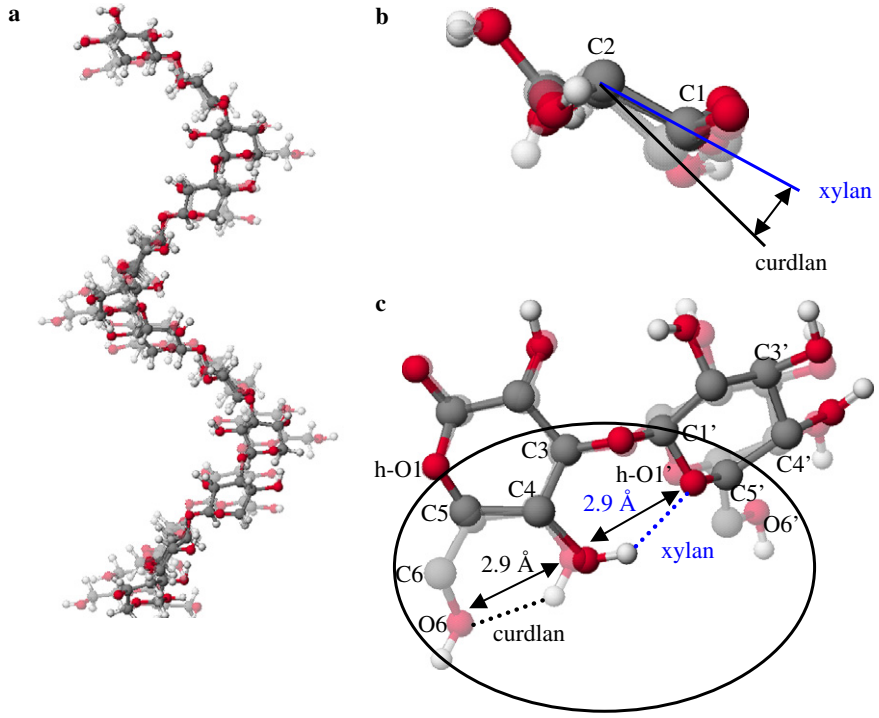

Fig. 4. Comparison between xylan and curdlan. Curdlan is drawn in half-transparent colors. (a) The side views of the helix. (b) Side view of one pyranose ring to show the tilting angle (c) the intra-ring hydrogen bond between O4 and O6 in curdlan and the inter-ring hydrogen bond between O4 and O1 in β-1,3-D-xylan.

the helix pitch of β-1,3-D-xylan is slightly shorter than that of curdlan; 17.55 Å of β-1,3-D-xylan and 17.61 Å of curdlan. This difference is related to the tilting angle of the pyranose ring as presented in Fig. 4(b), where the side views of the pyranose ring are overlaid. The pyranose ring of curdlan is more titled toward the helix axis than that of β-1,3-D-xylan.

The most difference between two conformations is made by the presence of C6 in curdlan. In curdlan, O4 can form an "intra-ring" hydrogen bond with O6. In contrast, O4 in xylose cannot form such an intra-ring hydrogen bond and thus makes an "inter-ring" hydrogen bond with the hemi-acetal oxygen in the adjacent pyranose ring (h-O1). The intra-ring hydrogen bond in curdlan does not influence the rotational angles of β-1,3 linkage. On the other hand, the inter-ring hydrogen bond should give perturbation to the angles. This would be the main reason for the difference in the parameters listed in the inset table in Fig. 1.

4. Conclusion

This paper examined the hydrogen bonds in the β-1, 3-D-xylan triple helix. These were three possible models (Types A, B, and C in Fig. 2). When we started the MOPAC optimization from Type A, it always converted to Type C. Type C stayed at Type C. On the other hand, Type B converted into Type RC which is very close to Type C. Both types can be categorized into an inter-chain and hydrogen-bond array type, being consistent the experimental facts.

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