Studies of crystalline native cellulosines using potential energy calculations

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Energies for various trial packing arrangements of unit cells for the Iα and Iβ phases of native cellulose discovered by Sugiyama et al. were evaluated. Both a rigid-ring method, PLMR, and the full-optimization, molecular mechanics program, MM3(90), were used. For both phases the models that had the lowest PLMR energy also had the lowest MM3 energy. Both calculated models have the chains packed ‘up’, O6s in tg positions, and the same sheets of hydrogen-bonded chains. The Iβ structure model is essentially identical to that proposed previously for ramie cellulose by Woodcock and Sarko. It is also the same as the best parallel model previously proposed that was based on the X-ray data of Mann, Gonzalez and Wellard, once the various unit cell conventions are considered. Also, the energies from both methods for all three celluloses, Iα, Iβ and II, are in the order that rationalizes their relative stabilities.

KEYWORDS: cellulose I, molecular mechanics, crystal structure, molecular, modelling

INTRODUCTION

The two main forms of cellulose are I, the major native type, and II, which occurs after mercerization or regeneration. A proposal for the solid-state conversion from I into II, including different intermediates, is described elsewhere (Nishimura et al., 1991, Nishimura and Sarko, 1991). Some years ago it was discovered (VanderHart and

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Atalla, 1984, Atalla and VanderHart, 1984) that native cellulose occurs mostly as combinations of the two phases, \( \alpha \) and \( \beta \). Depending on the sample, these phases are in different ratios. For example, the ratio \( \alpha:\beta \) was estimated to be 65%:35% for Valonia cellulose (VanderHart and Atalla, 1984). Initially, electron diffraction patterns from this mixture were indexed based on an 8-chain unit cell (Honjo and Watanabe, 1958). More recently, however, electron diffraction from small selected areas of the same microfibril showed two patterns that were interpreted to have, respectively, one-chain triclinic and two-chain monoclinic unit cells (Sugiyama et al., 1991). One of the most important conclusions from the finding of a 1-chain unit cell is that the chains must have a parallel orientation, i.e. the reducing ends of the cellulose molecules must all be at the same end in a given microfibril. Because both phases are found within the same microfibril in that work, the conclusion of parallel packing for \( \beta \) is more probable.

Several decades ago, Rånby (1952) showed that cellulose \( \beta \) is slightly more stable than cellulose \( \alpha \), by about 2 cal g\(^{-1}\) or 0.3 kcal mol\(^{-1}\) of glucose residues. Because hydrothermal annealing converts mixtures of \( \alpha \) and \( \beta \) into pure \( \beta \) (Horii et al., 1987), it is thought that \( \beta \) is more stable than \( \alpha \). As X-ray diffraction intensity data for the pure phases of native cellulose are yet not available, it is reasonable to propose structures based on energy calculations. This is especially so for \( \alpha \), because of the limited number of variables that must be considered for a 1-chain model, and our preliminary results for \( \alpha \) have already been published (Aabloo and French, in press).

In the present work various possible model structures for the \( \alpha \) and \( \beta \) celluloses were studied, based on published unit cell dimensions and on calculated packing energy. These results are compared with other work.

**METHODS**

All our computer models consisted of parallel chains and were based on published unit cell dimensions (Sugiyama et al., 1991). For \( \alpha \), \( a = 0.674 \) nm, \( b = 0.593 \) nm, \( c = 1.036 \) nm, \( \alpha = 117^\circ \), \( \beta = 113^\circ \) and \( \gamma = 81^\circ \), and for \( \beta \), \( a = 0.801 \) nm, \( b = 0.817 \) nm, \( c = 1.036 \) nm, \( \alpha = 90^\circ \), \( \beta = 90^\circ \) and \( \gamma = 97.3^\circ \). Space group \( P1 \) was used for the \( \alpha \) form, and the cellulose \( \beta \) chain models conformed to space group \( P2_1 \). Two different methods were used to calculate packing energies, PLMR and MM3. The PLMR (derived from \textit{polymer}) program, the previous version described by Pertsin et al. (1984) and Pertsin and Kitaigorodsky (1987), uses a 'rigid-ring' strategy. In PLMR models of the cellulose chains, most of the intraresidue parameters of the glucose rings are kept at average values reported by Arnott and Scott (1972). Only the exocyclic torsion angles \( \tau_i \) (cis = 0\(^\circ\), see Fig. 1) that locate the hydroxymethyl and three hydroxyl groups were varied. The chains were also free to rotate about their axes in the unit cell. For \( \alpha \), the torsion angles and bond angles at the glycosidic linkages were allowed to vary. For \( \beta \), the monomer residues were linked to form the chain with the variable virtual bond method (Zugenmaier and Sarko, 1980). Keeping \( 2 \) symmetry requires an additional parameter that characterizes the chain conformation. This is an angle that describes rotation of the monomer residue about the O4—O4' virtual bond. PLMR uses periodic boundary conditions and continuous chains to build up a crystal structure.

Model cellulose crystals for the MM3(90) (Allinger et al., 1989, Allinger et al., 1990) calculations were built of seven cellotetraose molecules which represented the very long