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A molecular modeling approach to understand conformation–functionality relationships of galactomannans with different mannose/galactose ratios

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ABSTRACT

Conformations of simulated galacomannans with different mannose/galactose ratios were investigated using molecular modelling software (Insight II/Discover_3 and RIS program, Version 4.0.0). The mannose/galactose ratios used in the present study were 4/1, 3/1, 2/1 and 1/1 respectively to simulate locust bean gum, tara gum, guar gum and fenugreek gum. Conformational parameters, Lp, C_∞ and Rg, were calculated. The results showed that the insertion of galactosyl groups could cause bending of the chains. The conformation of locust bean gum was much stiffer than the other three gums. Among the other three gums, fenugreek gum behaved as the most compact and flexible chain which might be due to the interactions along the side groups; guar gum behaved as the stiffest chain among the three gums, and tara gum was in the middle range. No ordered structures were observed in the fully substituted fenugreek gum chain. It was assumed that intra-chain interactions, both through side groups or smooth regions, could affect chain conformations. The results could explain the synergistic interactions between galactomannans and cellulosic polysaccharides: a more flexible chain can help with penetrating through networks in solutions, while the side groups can help with forming stronger "hyperentanglements" which themselves could increase viscosity; the stiffer chain with more unsubstituted regions can form junction zones with the cellulosic molecules.

1. Introduction

Galactomannans (GMs), a group of neutral polysaccharides naturally occurring in the seeds of some legumes, consist of a mannan backbone, with α-glactose at C6 of mannose (Dea, Clark, & McCleary, 1986). There are four primary plant sources of GMs, i.e. locust bean or carob tree (*Ceretonia siliqua* L.), guar (*Cyamopsis tetragonolobus* L. Tabu.), tara plant (*Caesalpinia spinosa*) and fenugreek (*Trigonella*). Galactomannans from these four plant sources give distinctive structural characteristics, generally, the mannose to galactose ratio (M/G) varies from 4:1, 3:1, 2:1 and 1:1 for locust been gum (LBG), tara gum (TG), guar gum (GG) and fenugreek gum (FG) respectively (Dea & Morrison, 1975). GMs are used widely in food, pharmaceutical and cosmetic industries as stabilizers and emulsifiers due to their high water binding capacity, emulsification properties and easy-to-form synergistic interactions with other components such as carbohydrates or proteins thus increasing viscosity (i.e. Bresolin, Sander, Reicher, Sierakowski, Rinaudo, & Ganter, 1997; Bresolin, Milas, Rinaudo, Reicher, & Ganter, 1999; Cui, Eskin, Biliaderis, & Mazza, 1995; Sudhakar, Singhal, & Kulkarni, 1996; Goff, Ferdinando, & Schorsch, 1999; Tavares, Monteiro, Moreno, & Lopes da Silva, 2005). In addition to the physical properties, GMs also contribute important health benefits for preventing or slowing the onset of chronic diseases (Cui, Ikeda, & Eskin, 2007). The synergistic interactions of GMs with cellulosic materials such as xanthan gum and non-pectic polysaccharides (NPP) from yellow mustard mucilage are vastly investigated (i.e. Cui, 2001; Cui, Eskin, Wu, & Ding, 2006; Cui et al., 1995). In a recent study (Wu, Cui, Eskin, & Goff, 2009a) we proposed that two mechanisms may co-exist to explain the synergism between GMs and NPP: the "junction zone" model and the segregative association model. The "junction zone" model has been well accepted for polymers with long unsubstituted smooth regions. However, this mechanism alone cannot explain the polymers with fully or partially substituted chains. Instead, the segregative association model can be a good alternative to explain the synergistic behaviour between fully or partially substituted polymers like FG or GG with NPP. The fine structure of GM molecules, including M/G ratio,

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galactose distribution pattern along the backbone, as well as its orientation, may greatly affect the conformation of the polymer, and the behaviour of its solution properties and interactions with other molecules (Bergamini, Boisset, Mazeau, Heyraud, & Taravel, 1995; Mazeau & Rinaudo, 2004; Viebke & Piculell, 1996). It still remains a major challenge to understand the "fine structure"-conformation relationship due to the difficulty in obtaining information on the fine structures. However, computer simulation of molecules with specific fine structures of various distribution patterns and orientations is a superior and effective technique for comparing the conformational characteristics with the experimental data. Molecular modelling has become a unique and indispensable tool by proving invaluable conformational information complementary to the data obtained experimentally (Rao, Qasba, Balaji, & Chandrasekaran, 1998).

Computer simulation of galactomannan chains has been investigated by a number of researchers using various approaches, i.e. Bergamini et al. (1995) investigated the conformational properties of oligo-galactomannans using MM3 force field and compared their data with NMR results. Chandrasekaran and Radha (1997) studied the geometrical characteristics of galactomannans chains and found a good agreement with data obtained from X-ray diffraction. Mazeau & Rinaudo, 2004, Petkowicz, Reicher, and Mazeau (1998) and Petkowicz et al. (1999) systematically studied the conformation of GM chains with different M/G ratios using MM3 force field and predicted the stiffness and the flexibility of these chains. In the present study, GMs with M/G ratios of 4, 3, 2 and 1 were built to simulate the materials used in our previous studies (Wu et al., 2009a Wu, Cui, Eskin, & Goff, 2009b;) with the conformational parameters calculated by the molecular modelling software. The objectives of the current study were to investigate how M/G ratios of GMs affect chain conformations and corresponding functionalities, and to understand the mechanism responsible for synergistic interactions with other polymers.

2. Materials and methods

2.1. Materials

In order to simulate the materials examined in the previous studies, GM molecules with corresponding M/G ratios, 4/1, 3/1, 2/1 and 1/1 were built to represent the following materials investigated in our previous studies, LBG, GG, TG and FG.

2.2. Molecular modelling methods

2.2.1. Molecular models and force fields

Molecular modeling calculations were performed on Insight II/Discover_3 and RIS program (Version 4.0.0, Molecular Simulations Inc., San Diego, USA) and a silicon Graphic O2 workstation.

Simulations were performed with a dielectric constant of 4.0 for all calculations. This value was believed to be the most appropriate from comparisons of the D-glucopyranose ring with crystal structures (French, Rowland, & Allinger, 1990). It was used to obtain better agreement with experimental values in aqueous solutions (Homans, 1990). Although high dielectric constants like $\varepsilon = 80$ were used by many researchers for better comparisons with experimental data, a low dielectric constant ($\varepsilon = 4$ in the present study) was preferred over a high dielectric constant after comparing several adiabatic maps using some sharply different dielectric constants. Stortz (1999) stated that using low dielectric constants could result in a good approximation to the true adiabatic map, while high dielectric constants could damp the electrostatic and hydrogen-bonding interactions (Stortz, 1999).

The AMBER force field applied contained a correction for the anomeric and exo-anomeric effects and has been adapted for generating of adiabatic contour map of epimelibiose (α, 1-6 linked galactose to mannose), and for minimization of energy of polysaccharide chains. After energy minimization of polysaccharide chains, the consistent valence force field (CVFF) was applied for Rotational Isomeric State-Motropolis Monte Carlo (RMMC) calculation of conformational parameters.

2.2.2. Nomenclature

The recommendations and symbols proposed by the Commission on Nomenclature (McNaught, 1997) are used throughout this paper. The following torsion angles describe the relative orientations of a pair of contiguous residues,

φ = O5'–C1'–O6–C6

ψ = C1'–O6–C6–C5

The orientation around the C5–C6 bond is defined by

ω = C4–C5–C6–O6

The primed atoms correspond to the non-reducing residue (α-galactose) and the unprimed atoms correspond to the reducing one (β-mannose) (Fig. 1).

2.2.3. Generation of adiabatic contour map (φ-ψ map) of epimelibiose

The stable chair $^4C_1$ conformation has been applied for the pyranose monosaccharide rings. The hydroxymethyl groups had either gauche–gauche (*gg*), gauche-trans (*gt*) or trans-gauche (*tg*) orientations (relative to the ring C-4 and O-5 atoms, respectively), with their hydroxyl hydrogen atoms oriented to weakly hydrogen bond with the ring oxygen atoms. Clockwise (C) or reverse clockwise (R) orientations were chosen for the secondary hydroxyl groups. Twenty-four starting conformations of epimelibiose were applied with *gt*, *gg* or *tg* orientation of the hydroxymethyl groups. The conformations of epimelibiose were explored by systematically stepping the glycosidic φ and ω torsion angles from -180° to 180° with 20° increments. At each point, energies were calculated after energy minimization with restrains for those φ and ψ torsion angles, but while allowing the other variables to relax.

2.2.4. Polysaccharide chain building

Repeat units, epimelibiose and mannose, are randomly linked through mannopyranosyl residues *via* β-1,4 linkages with the appropriate epimelibiose/mannose ratio to represent corresponding

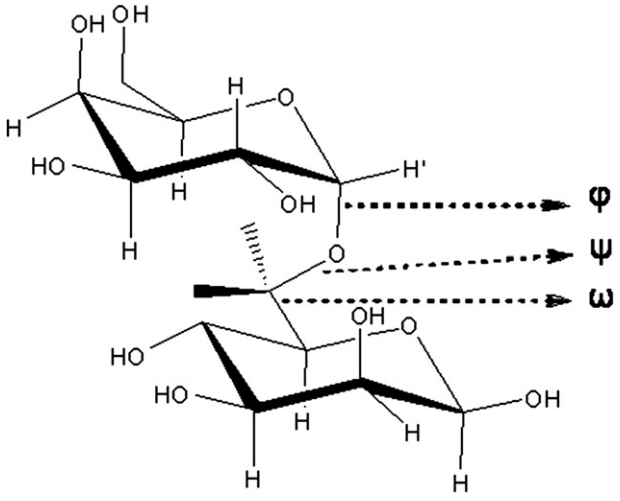

Fig. 1. Schematic representation of epimelibiose and torsion angles.