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Molecular mechanics of arabinoxylan oligomers

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Arabinoxylans are main components of the primary cell wall in Gramineae and also are minor components of the secondary cell wall of dicots. The molecule consists of a linear chain of (1→4)-β-xylanopyranosyl units substituted by α-L-arabinofuranosyl residues at O(2) and mainly at O(3) atoms of xylose. There is also a significant proportion of xylose substituted at both O(2) and O(3) atoms. Arabinosylation of xylan affects conformation and both physical and biological properties of the polymer. The properties depend on the number of arabinofuranose substituents and their distribution along the main xylan chain.

The authors attempted to determine low energy conformations of pentaxylose oligomers substituted by arabinofuranose residues at various positions. The TRIPOS SYBYL program was used and conformation search was performed with the TRIPOS force field (see SYBYL Theory Manual, TRIPOS, 1992).

The three superimposed structures in Fig. 1 represent three low energy conformations of unsubstituted pentaxylose chain found by searching a set of randomly generated conformations. All three conformations are characterized by the heat of formation (HOF) values differing by less than 4.7 kcal/mole — well under the thermal vibrations energy at the normal temperature. The conformations shown represent a small portion of 112 conformations differing in HOF by at most 9 kcal/mole. This result shows a great flexibility of unsubstituted oligoxylans.

Arabinosylation of oligoxylans reduces significantly its flexibility. Only 52 low energy conformations were found for the pentaxylose substituted at O(2) and O(3) atoms of the second and third xylose by arabinose residues. All these conformations exhibit more prominent helix-like twisting of xylose backbone with arabinose residues protruding outside this helix (Fig. 2).

Both unsubstituted and substituted oligoxylans exhibit a significant dipole-like electrostatics resulting from asymmetry of glycoside

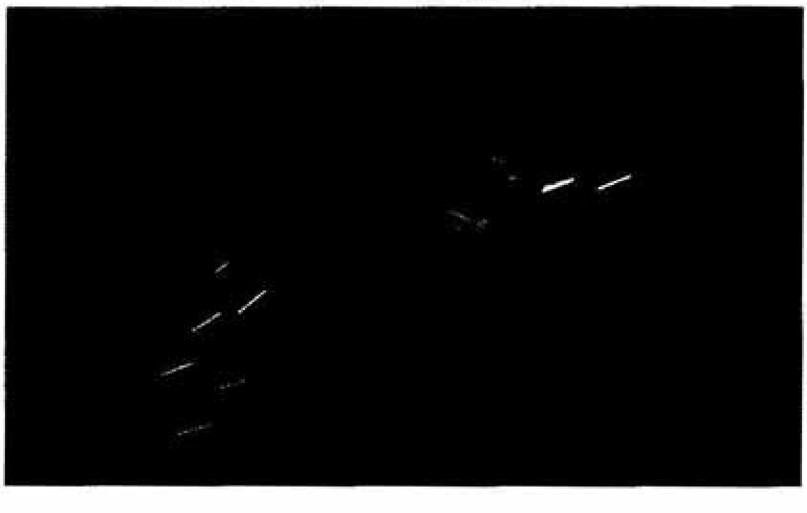

Fig. 1. Three low energy pentaxylose conformations superimposed at the central xylose residuum.

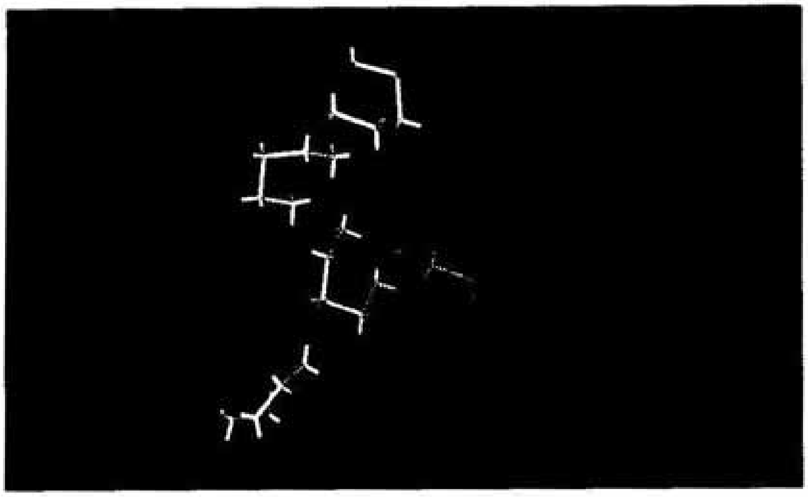

Fig. 2. A typical low energy conformation of O(2), O(3); O(2), O(3) Ara_4 - Xyl_5.

Fig. 3. Isopotential surfaces around unsubstituted pentaxylose.

Fig. 4. Isopotential surfaces around O(2), O(3)- Ara_2-Xyl_5.

bonds: residues linked to an anomeric carbon are positively charged while other residues are charged negatively. Electrostatic potential maps for unsubstituted and substituted pentaxylose are given in Fig. 3 and Fig. 4.

The simulations presented did not take into account hydratation which induces stabilization of the molecule. Full flexibility analysis requires however, long time runs to measure molecular dynamics with the solvent taken into account. Such runs are impossible at currently available hardware, but are planned for the near future.