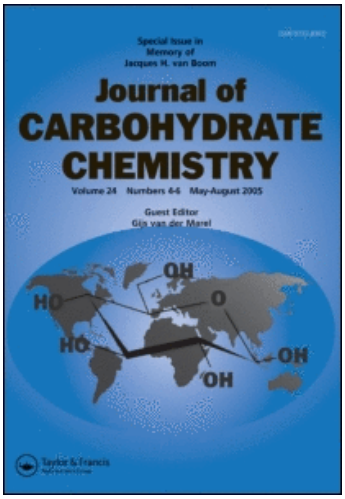

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COMMUNICATION

SYSTEMATIC ESTIMATES FOR POSSIBLE REGULAR HELIX MODELS OF HETEROPOLYMERIC GLUCANS, ELSINAN AND LICHENAN, USING *N-H* MAPPING METHOD

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Regular helical structures of polysaccharides are most conveniently described by a set of the helix parameters; *n* for the number of chemical repeating units per turn and *h* in Å for the rise per unit along the helix axis. A two dimensional mapping of *n-h* values for possible helix models along with the potential energy surfaces allows one to estimate conformational accessibility of a given posaccharide.[1-3] Recently, we have adopted the method to study an acidic heteropolysaccharide[4] and a branching glucan.[5] These polysaccharides involve two or three sets of backbone glycosidic linkages (Φ-Ψ), each of which varies independently, and, therefore, enormous multidimensional spaces must be explored. Their *n-h* maps were calculated based on the low energy Φ-Ψ values derived from MM3[6-8]-generated, relaxed-residue potential energy maps[9, 10] of the component disaccharides. The present assessment of helix models for the two heteropolymeric glucans is achieved by calculating *n-h* maps in a similar fashion. These glucans are the two poly(disaccharide)s, poly[(1→3)-α-D-maltotriose] (elsinan) and poly[(1→3)-β-D-cellotriose] (lichenan). In addition to single-stranded helices, three types of mutiple helices; double-parallel, and double-antiparallel, and triple helices have also been examined.

The disaccharides studied by the MM3 relaxed-residue energy map calculations were methyl-*O*-α-nigeroside, methyl-*O*-α-maltoside, methyl-*O*-β-laminarabioside, and methyl-*O*-β-cellobioside. The dielectric constant was set to be 4.0 when partially optimizing the disaccharides with fixed Φ-Ψ angles. All energy maps were constructed with a 10° grid space of Φ-Ψ angles. Regular helix models were constructed by a succession of glucose residues based on fixed geometry and sets of Φ-Ψ values. The standard D-glucopyranose residue[11] was used and hydroxyl hydrogen atoms were not included. The three sets of Φ-Ψ values were taken from the low MM3 energy region—less than 3 kcal/mol from the global minimum. In the present calculations, the virtual bond[12] was a vector between terminal glycosidic oxygens of a repeating trisaccharide unit instead of a monomer. The trisaccharide repeating unit in helix models sometimes covered beyond a 180° range about the helix axis and, therefore, models with $0 < n < 2$ had to be taken into account. The energy of each resulting model was evaluated based on the Lennard-Jones type nonbonded potential functions for van der Waals[13] and hydrogen bond interactions,[14] the exo-anomeric effect function for Φ rotations,[15] and sinusoidal three-fold functions with the eclipsed rotational barrier of 1 kcal/mol about Φ-Ψ rotations. A threshold energy value to distinguish an acceptable model from others was defined to be 0 kcal/mol; those having attractive total energies were selected for the following *n-h* mapping. *N-H* maps of possible helix models were depicted based on the *n-h* points with grid-averaged, energy- and population-weighted density. The procedure of the *n-h* mapping was described in our previous report.[5] Briefly, a whole *n-h* range was divided into a small rectangular region with an arbitrary size 0.4 (n)×0.4 (h in Å). The *n-h* distributions of the models belonging to each region were represented by the percentage of Boltzman averaged density, ρ, following;

$$\rho = \frac{q}{Q} \times 100 \quad \text{where } q = \sum_{r}^{n} \exp\left(-E_r / RT\right)$$

In the expressions, q is the regional partition function of the models present in each region and Q is a total partition function given by summing the individual partition function. E_r is the steric energy of the r-th model in the region. The temperature T was set to be at 298K.

Figure 1 shows the *n-h* maps of single helix models of the glucans. The preferred structures of the isolated chain of elsinan (Figure 1-a), suggested by the highest density point with 6%, are tight, right-handed helices with $n = 1.4$, while their h values are around 10 Å. This major peak comprises all the iso-density contour lines more than 1%, while the 0% contour lines cover most of the *n-h* regions shown in the map. The tiny second peak consisting of the 1% contour line appears $n = -3.4$ and $h = 10.6$ Å. The X-ray diffraction data of elsinan included two reflections that appeared to be on the meridian, having spacings of 15.1 Å and 8.9 Å.[16] These reflections were indexed with (003) and (005) for the fiber repeat distance of about 45 Å. On this basis, a right-handed, single helical tight structure having $n = 1.25$ or 1.67, namely, 5_4 or 5_3 helices, with h about 9 Å is most probable. On the other hand, as shown in Figure 1-b, the single helix map of lichenan has quite a different appearance. A major peak having the highest point appears at the region for right-handed helices and a lower peak is found in the left-handed helix regions. The peak density of the former, located at $n = 2.6$ and $h = 13$ Å, reaches only 0.84%. The *n-h* pattern suggested that the single helix models are more equally populated over the allowed *n-h* regions, indicating an intrinsic flexibility of the glycosidic linkages of a lichenan chain. A conformational analysis of lichenan suggested a right-handed, three-fold helix with the fiber repeat distance 42.03 Å.[17] The reported *n-h* value, $n = 3$ and $h = 14.01$ Å, is well near to the major peak at the positive n region.

The *n-h* maps in Figure 2 compare the single, double, and triple helices maps of the glucans, where the iso-density contour lines more than either (a) 1% or (b) 0.5% are only drawn for clarity. The double helix map comprises both parallel and antiparallel models. In Figure 2-a of the elsinan map, the centers of multiple helix peaks are in the region for more collapsed, wider helical structures than that of the single helix peak. As for possibilities of multiple helical structures, the peak regions of the double and triple helices are reasonably in agreement with 5_2 and 5_1 helices ($n = 2.5$ and 5), respectively. The superimposed map of lichenan in Figure 2-b shows several sharp peaks for multiple helices appearing at low h regions (< 4 Å). Such collapsed helix models derived from the peaks are obviously unrealistic. More important peaks for multiple helices are found near the major peak of the single helix models since they are fairly close to the observed *n-h* values. These multiple helix peaks have slightly smaller h values than the single helix peak. The X-ray structure of lichenan showed that two single helices were packed in the

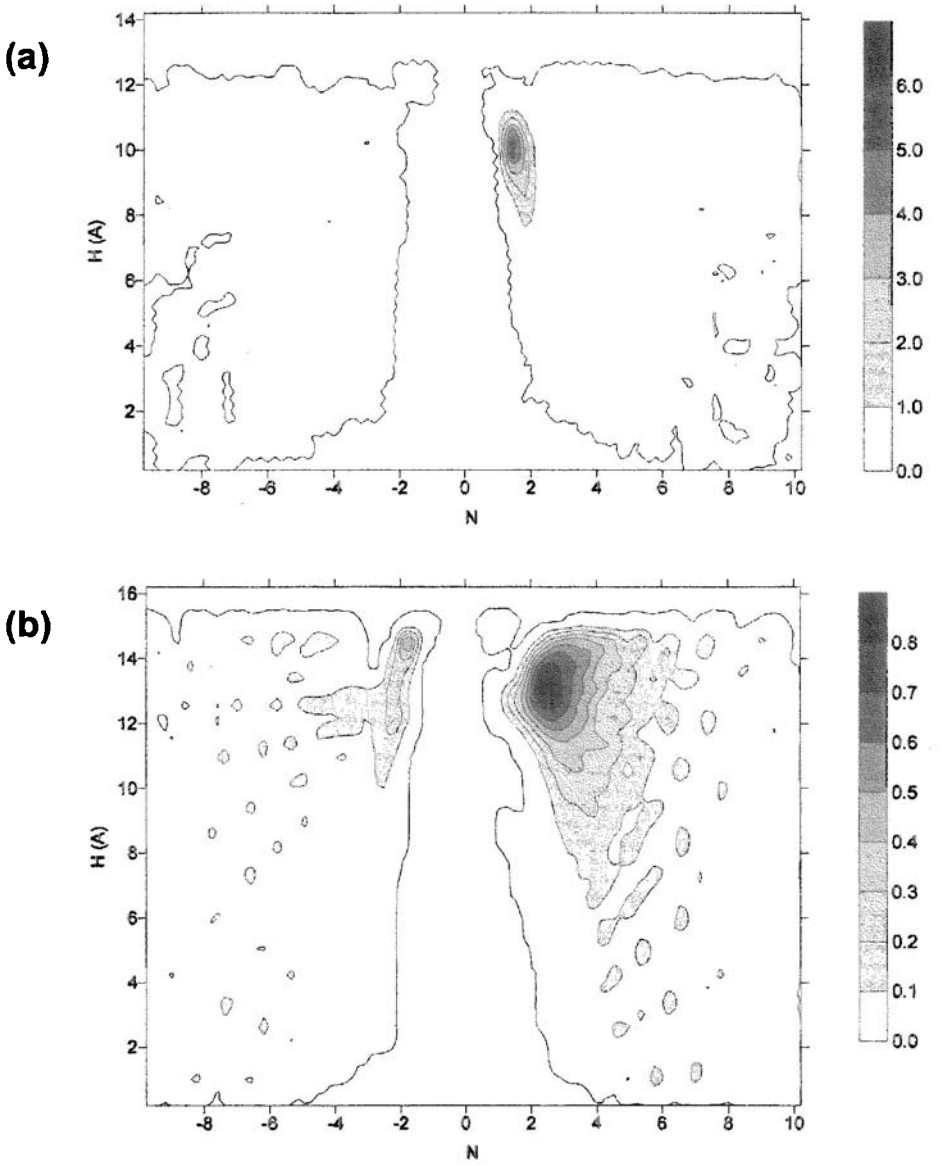

Figure 1. *N-H* maps of elsinan (a) and lichenan (b). Iso-density contour lines are generated in 1% increments (a) or 0.5% increments (b).

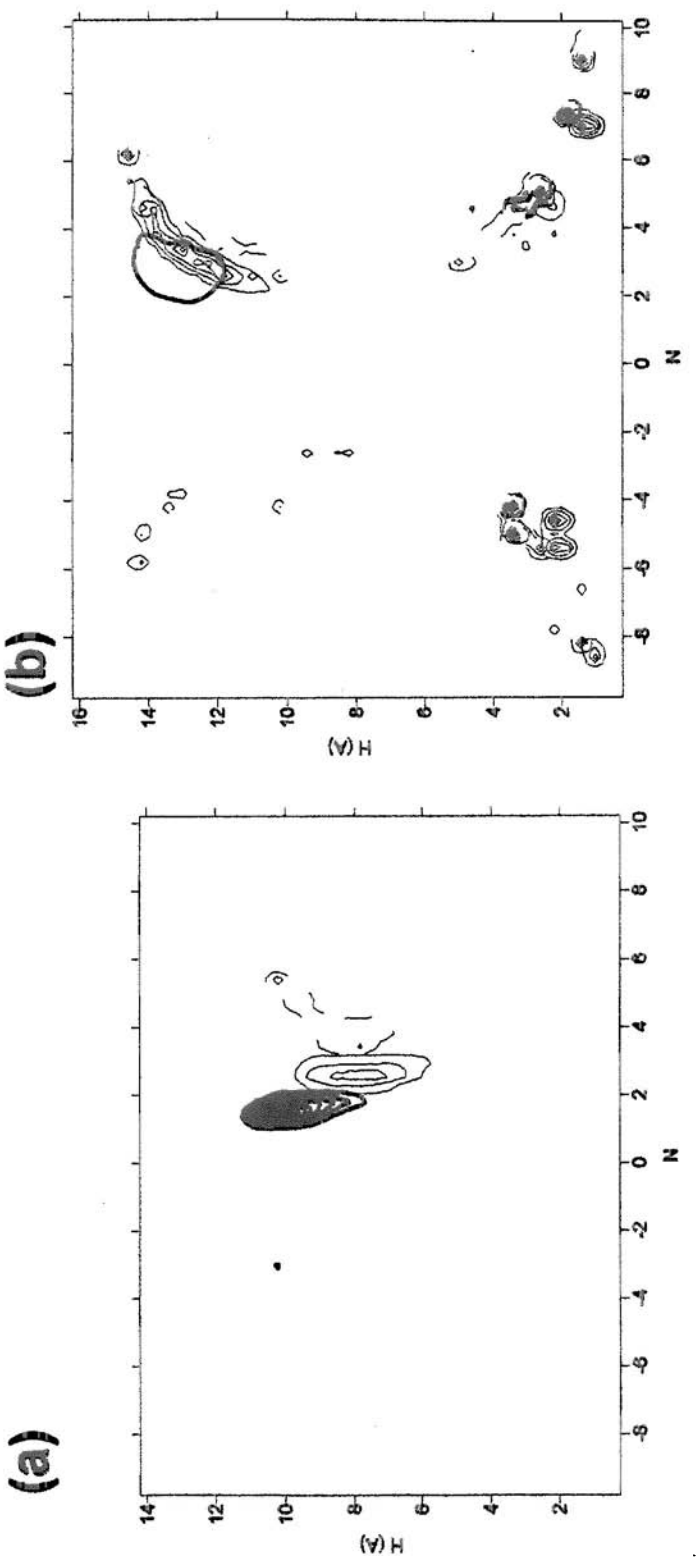

Figure 2. Superimposed *n-h* maps of single and multiple helices of elsinan (a) and lichenan (b). Iso-density contour lines are generated in 0.5% increments and contours more than 1% (a) or 0.5% (b) are drawn for clarity. Thick, thin, and broken contours correspond to single, double, and triple helices, respectively.

unit cell with antiparallel polarity; this was determined by a stereochemical packing analysis complemented with the space group symmetry.[17] This study also tested the packing model using a double helix and concluded it to be stereochemically unacceptable. However, our present calculation still suggests the possibility of formation of double helix strands as its X-ray structure.

The present *n-h* mapping study of two heteropolymeirc glucans, based on the region-averaged, energy and population weighted density, has successfully revealed their conformational features. The major peaks located in the *n-h* regions of the single helix maps and of the multiple helix maps are reasonably in agreement with the diffraction data. However, it is very likely that optimization of the helix models obtained from high density peaks would result in diverse structures, each having similar steric energies, even if the observed helical symmetries are imposed. However, the crystal structures of the two glucans have not been determined completely due to poor qualities of their diffraction data. The helix models obtained by the present modeling study should rather be used for further re-examinations for their crystal structures based on the improved diffraction data, which includes a test for multiple helix models.

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The expression of hydrogen bond energy is given by :

$$E_{hb} = 33.14(r\text{-}2.55)(r\text{-}3.05),$$

where r is the distance between oxygen atoms.
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The expression of the exo-anomeric effect for the glycosidic ϕ rotations (β-form) is given by :

$$E_{eae} = 0.07(1\text{-}\cos\phi)\text{-}0.368(1\text{-}\cos 2\phi)\text{+}0.573(1\text{-}\cos 3\phi)\text{-}0.958\sin\phi\text{ -}0.107\sin 2\phi$$

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