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Modelling of arabinofuranose and arabinan. Part 1: conformational flexibility of the arabinofuranose ring

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ABSTRACT

The conformational behaviour of methyl β-D- and methyl α-L-arabinofuranosides have been assessed through computations performed with the molecular mechanics program MM3 using the flexible residue method. Energies for various envelope and twist conformers were calculated as a function of the puckering parameters Q and ϕ. The gauche–gauche, gauche–trans, and trans–gauche orientations of the primary hydroxyl groups at C-5 were accounted for. Our calculations provide some insight into extensive conformational flexibility that both molecules display and shed light on the possible pathways for conformational interconversions. Both molecules display very characteristic conformational behaviour. The conformations of methyl β-D-arabinofuranoside, which have been determined by single-crystal X-ray diffraction studies, are distributed in two fairly deep low-energy wells. These conformations are no more than 1.5 kcal/mol above the respective energy minima. In the case of methyl α-L-arabinofuranoside, crystallographic data are lacking and only ^1H–^1H coupling constants are available. Using suitable equations for the H–C–C–H segments, the theoretical $^3J_{H-H}$ coupling constants were calculated as a function of the two puckering parameters, taking into account all the accessible conformations. Agreement with the experimentally reported data confirms the high flexibility of furanose rings in solution.

INTRODUCTION

Arabinose is widely distributed in Nature in both D and L forms. The tautomeric composition of the arabinose monomer depends upon the solvent[1]. The oligomers and polymers present in plants usually contain the L-arabinofuranose form. Arabinans and arabinoxylans of plant cell walls are of the α-L type[2,3], whereas the glycan moiety of hydroxyproline-rich glycoproteins such as "extensins" consists of β-L-arabinofuranose[4]. β-D-Arabinofuranoside is a constituent of natural nucleoside analogs with antiviral activities[5]. Since nucleosides prepared with β-D-arabinofuranose are potent DNA binders, numerous crystallographic data are available for this enantiomer.

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In contrast to pyranose carbohydrate rings that usually have a stable ring conformation, furanose rings are known to display high flexibility. Five-membered rings can usually adopt a large number of conformations that are referred to as twist and envelope forms. The pseudorotation path which allows interconversion from one shape to another presents almost no energy barriers in the case of cyclopentane[6,7]. When the methylene groups are replaced with heteroatoms and/or these carbons bear substituents, some of the conformers become energetically favoured. Up to now, only two families of furanose rings have been extensively studied on a theoretical basis. The conformational analysis of fructofuranose, a ketohexose, has been carried out by means of molecular mechanics methods[8,9]. More extensive studies, either by molecular mechanics or quantum chemistry methods, have been done on the aldopentoses, ribose, and deoxyribose, since these sugars are constituents of nucleic acids, and their conformation affects the DNA or RNA helical conformation[10].

Some theoretical calculations have been performed on arabinonucleotides[11,12], but a complete analysis of the arabinofuranose conformational behaviour has not been reported. In a recent NMR study of the arabinose moiety of wheat arabinoxylan[13], the coexistence in solution of two families of pseudorotamers was proposed. In the present study, the arabinofuranose ring conformational behaviour has been investigated by means of molecular mechanics methods. The results are compared with crystallographic data obtained on β-D-arabinosides. For the α-L-arabinofuranose, theoretical coupling constants have been calculated and are compared to experimental data obtained for (1 → 5)-α-L-arabinobiose[14] and arabinoxylan fragments[13].

MATERIALS AND METHODS

Nomenclature.—The recommendation and symbols proposed by the Commission on Biochemical Nomenclature are used throughout this paper[15]. Schematic representations of methyl β-D-arabinofuranoside (**1**) and methyl α-L-arabinofuranoside (**2**), along with the atomic labels of interest, are displayed in Fig. 1. The hydroxymethyl group orientation is described by the torsion expression,

$$\omega = \text{O-4–C-4–C-5–O-5} \qquad (1)$$

This group can adopt three staggered conformations, defined as gauche–gauche (*gg*), gauche–trans (*gt*) and trans–gauche (*tg*)[16]. In this system the first term refers to the relationship of the atom O-5 to O-4, and the second one to the relationship of the atom O-5 to C-3. For calculation of coupling constants, the torsion angle about the C-4–C-5 bond which is defined by the position of H-4 and one of the prochiral protons H-5 pro-*R* and H-5 pro-*S* (abbreviated as H-5*R* and H-5*S* throughout this paper), will be designated as either ω_{HR} or ω_{HS} where,

$$\omega_{HR} = \text{H-4–C-4–C-5–H-5}R \qquad (2)$$

$$\omega_{HS} = \text{H-4–C-4–C-5–H-5}S \qquad (3)$$

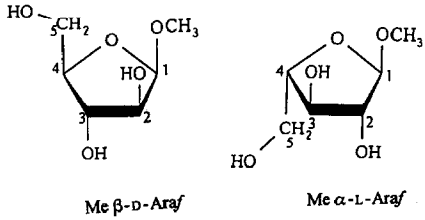


Fig. 1. Schematic representation of methyl β-D-arabinofuranoside (1) and methyl α-L-arabinofuranoside (2).

The three stable rotamers of the hydroxymethyl group of α-L-arabinofuranose, along with the definition of the torsion angles, are displayed in Fig. 2. It should be noted that the L and D series only differ in the sign of the torsion angles.

Molecular modelling.—Pucker definition and model building. Flexible ring shapes can be conveniently defined by the so-called pseudorotation parameters. Their description involves amplitudes, which measure the deviation from planarity, and phase angles that describe the type of distortion. One amplitude parameter and one phase angle are needed to characterize five-membered ring puckering. Two descriptions have been proposed[6,17] and recently compared[8]. The Cremer–Pople parameters[6] (Q, ϕ) are used throughout this paper. The relationship between the Cremer–Pople parameters[6] and the 20 different twist (T) and envelope (E) shapes that can be adopted by a five-membered ring are identified on the pseudorotation wheel displayed in Fig. 3.

As starting models for the molecular mechanics calculations, 121 arabinofuranose rings were built following the procedure previously described for the fructofuranose conformational study[8]. For each of the 10 envelope shapes, six rings were built using six displacements (0.3–0.8 Å) of one atom above (or under) the ring plane. In the case of twist shape, two atoms were displaced (six displacement values from 0.1 to 0.5 Å) in opposite directions. The planar ring was also constructed. The locations of the 121 starting models on the pseudorotational wheel have been represented in Fig. 3. The generation of the 121 starting models was repeated six times, since both β-D-arabinofuranose and the α-L enantiomer were studied, and in each case the three staggered orientations of the hydroxymethyl exocyclic group, (*gg*, *gt*, and *tg*) were considered. Starting distances and angles for the furanose ring were taken from crystallographic data[18].

Energy map calculations. The molecular mechanics program MM3[19,20] was used for all the calculations. This program takes into account the contribution of stretching, bending, stretch-bending, torsional and dipolar energies as well as Van der Waals interactions. The exo-anomeric effect is also included, and this program has been shown to be suitable for modelling carbohydrates[21]. A dielectric constant of 4.0 has been used to reproduce carbohydrate conformations in the crystal state.

(Calculated values for the atomic coordinates for both methyl α-L- and methyl β-D-arabinofuranoside are available from the authors.)

The three planar atoms of the starting ring models were made coincident with the *x-y* plane. Optimization was then performed while constraining only the *z* coordinates of the five ring atoms. The puckering parameters were calculated for each optimized conformation, since some deviation from the constrained values was possible during the energy minimisation. Pucker parameters calculations were done with a subroutine * including the equations from Cremer and Pople[6]. Potential energy surfaces could then be plotted as a function of the two puckering parameters.

Calculations of theoretical NMR parameters.—Coupling constants. For each ring conformation, three intracyclic coupling constants $^3J_{H1-H2}$, $^3J_{H2-H3}$, and $^3J_{H3-H4}$, respectively, were calculated using the following equations established by the method of Haasnoot and coworkers[22].

$$^3J_{H1-H2} = 3.083 \cos 2\Theta - 0.91 \cos \Theta + 0.927 \sin 2\Theta + 4.166 \quad (4)$$

$$^3J_{H2-H3} = 4.367 \cos 2\Theta - 0.91 \cos \Theta - 1.866 \sin 2\Theta + 4.995 \quad (5)$$

$$^3J_{H3-H4} = 4.416 \cos 2\Theta - 0.91 \cos \Theta + 0.097 \sin 2\Theta + 4.881 \quad (6)$$

It was then possible to plot the coupling constants as a function of the two puckering parameters. Such a drawing shows whether or not the coupling constants will be sensitive to the distribution of allowed conformations.

Using the same approach[22], the theoretical coupling constants, $^3J_{H4-H5S}$ and $^3J_{H4-H5S}$, were calculated for the three staggered orientations *gg*, *gt*, and *tg* of the exocyclic group. In the case of α-L-arabinose, the following system of equations (*7–9*) yields the mole fractions (P_{gg}, P_{gt}, and P_{tg}) for each of the rotamers.

$$2.90P_{gg} + 3.08P_{gt} + 10.79P_{tg} = {}^3J_{H4-H5R} \quad (7)$$

$$1.08P_{gg} + 10.79P_{gt} + 4.91P_{tg} = {}^3J_{H4-H5S} \quad (8)$$

$$P_{gg} + P_{gt} + P_{tg} = 1 \quad (9)$$

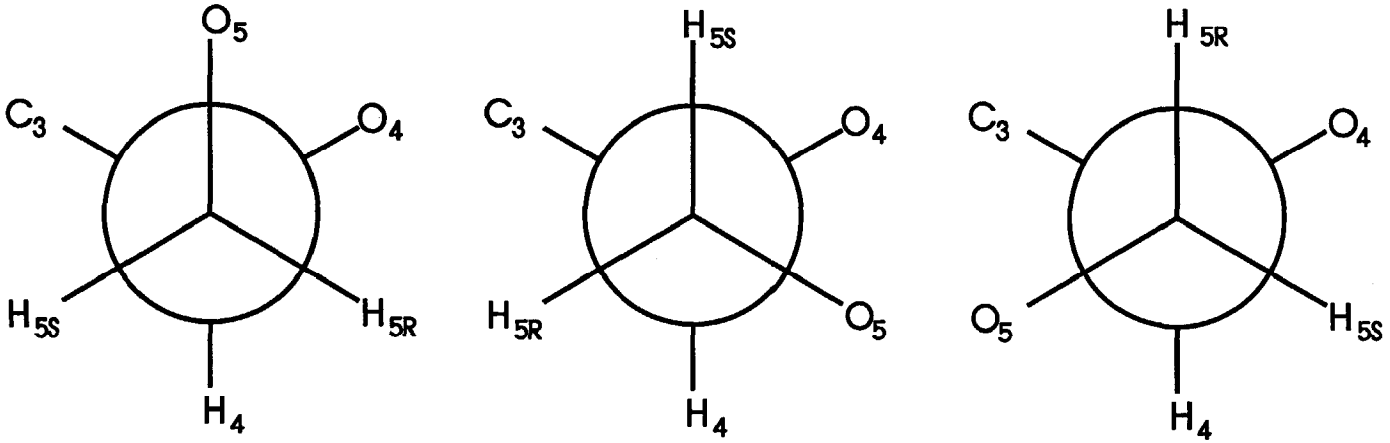
Averaging over the energy maps. In order to compare the intracyclic theoretical coupling constants with the experimental ones from (1 → 5)-α-L-arabinobiose[14] or arabinoxylan[13] it is necessary to average the theoretical values over all the possible conformations. Using the Boltzmann distribution, the relative population of each conformer is given by expression:

$$P_i = \exp(-E_i/kT) / \sum \exp(-E_i/kT) \quad (10)$$

The average coupling constants then can be calculated from all the individual ones by equation *11*.

$$\langle {}^3J_{H-H} \rangle = \sum P_i ({}^3J_{iH-H}) \quad (11)$$

* This subroutine was originally written by Dr. Larry Madsen (see ref. 8).



GG	GT	TG
ω = 60°	ω = -60°	ω = 180°
ω_{HR} = 60°	ω_{HR} = -60°	ω_{HR} = 180°
ω_{HS} = -60°	ω_{HS} = -180°	ω_{HS} = 60°
$^3J_{H4\text{-}H5R}$ 2.90 Hz	$^3J_{H4\text{-}H5R}$ 3.08 Hz	$^3J_{H4\text{-}H5R}$ 10.79 Hz
$^3J_{H4\text{-}H5S}$ 1.08 Hz	$^3J_{H4\text{-}H5S}$ 10.79 Hz	$^3J_{H4\text{-}H5S}$ 4.91 Hz

Fig. 2. Three stable rotamers for the exocyclic group of α-L-arabinofuranose. For each of the orientations, the values of the torsion angles along with the theoretical coupling constants are indicated.

RESULTS AND DISCUSSION

Energy map of the methyl β-D-arabinofuranose ring.—The energy maps of methyl β-D-arabinofuranoside have been calculated for the three orientations of the hydroxymethyl groups. For the three rotamers, two low-energy regions, called North (N) and South (S), can be located on the potential-energy surface. By reporting the lowest energy for each (Q,ϕ) value, a so-called "adiabatic" map is produced, see Fig. 4.

The North family of conformations comprises 5 pseudorotamers ($^1T_2$, E_2, $^3T_2$, ^3E, and $^3T_4$) within a 1 kcal/mol energy window. After unconstrained complete optimization, the lowest energy North conformer converges to a $^3T_2$ shape with $Q = 0.41$ and $\phi = 271.1°$ and is referred as β-D-North. The South low-energy region encloses seven pseudorotamers ranging from ^0E to E_3 in the 1 kcal/mol

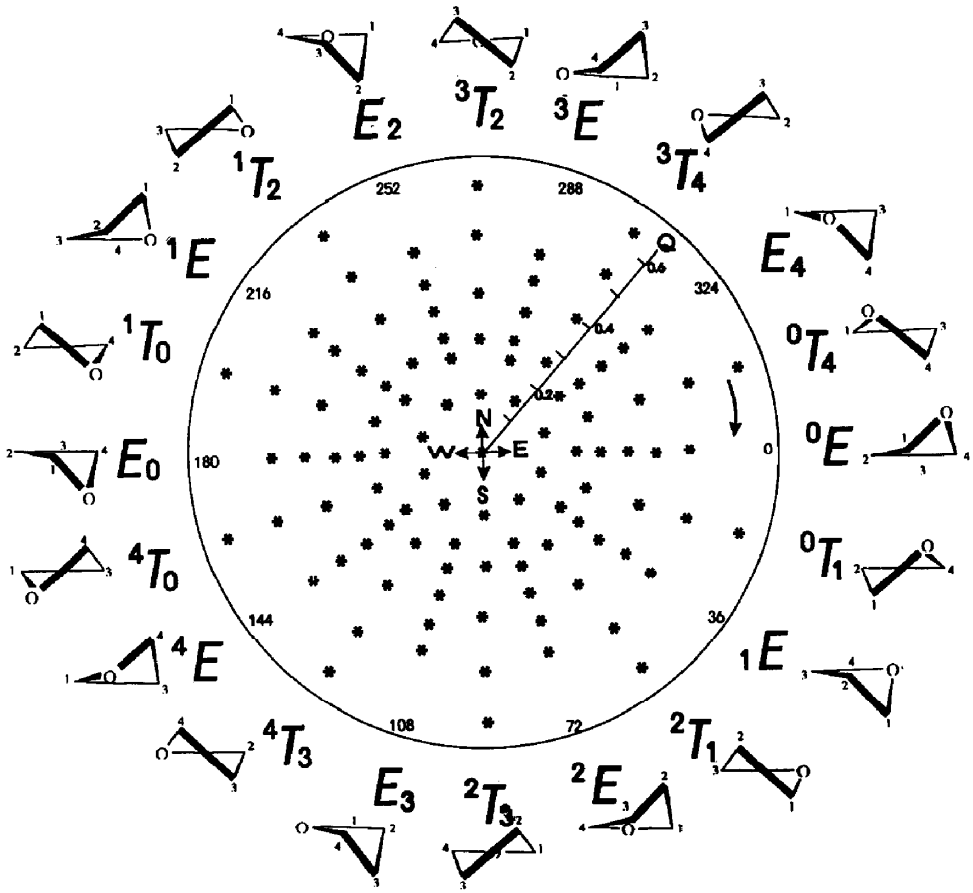


Fig. 3. Pseudorotational wheel of furanose rings along with the 20 twist and envelope shapes. The puckering parameters indicated are in accordance with the Cremer–Pople convention[6]. The stars on the surface indicate all the starting point generated for MM3 calculations.

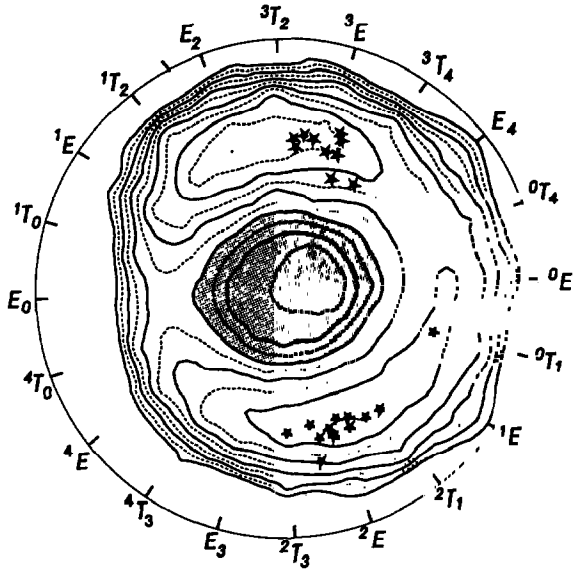


Fig. 4. Adiabatic pseudorotational energy surface of methyl β-D-arabinofuranoside as a function of the puckering parameters Q and ϕ. Isoenergy contours are drawn by interpolation of 0.5 kcal/mol with respect to the absolute minimum. Twenty-two ring conformations observed in crystal structures of β-D-arabinofuranose-containing molecules have been indicated by a star on the energy surface.

energy contour. The South minimum, after complete energy minimisation, adopts a $^2T_3$ conformation with Q = 0.36 and $\phi = 60.5°$ and is referred to as β-D-South. The β-D-South energy value is slightly higher (1.3 kcal/mol) than the β-D-North one. Both β-D-North and β-D-South pseudorotamers are displayed in Fig. 5. For both of them a *gt* orientation of the hydroxymethyl group is energetically preferred over a *gg* orientation by less than 2 kcal/mol. The literature was searched for crystal structures of β-D-arabinofuranose-containing molecules. In order to minimize the effect of substitution on ring distortion, only those having no more than one substituent were selected and analyzed. Their puckering parameters have been reported on the adiabatic map in Fig. 4. Among the 22 structures considered, 10 belong to the North family and 12 to the South family. As for the orientation of the primary hydroxyl groups, five adopt the *gg* orientation and 17 adopt the *gt* orientation, thus confirming the energy preference of the latter. With the exception of only one structure, all the observed puckering parameters lie within the 2 kcal/mol isoenergy contour. Such an agreement between theoretical conformers and observed crystal structures validates the use of MM3 for modelling the flexibility of five-membered carbohydrate rings.

From the above energy map, a facile pseudorotation can occur that involves almost all of the twist and envelope forms. Only the three pseudorotamers having their ring oxygen below the ring plane ($^1T_0$, E_0, and $^4T_0$) do not belong to 2 kcal/mol isoenergy contour. Therefore, the pathway for conversion between North

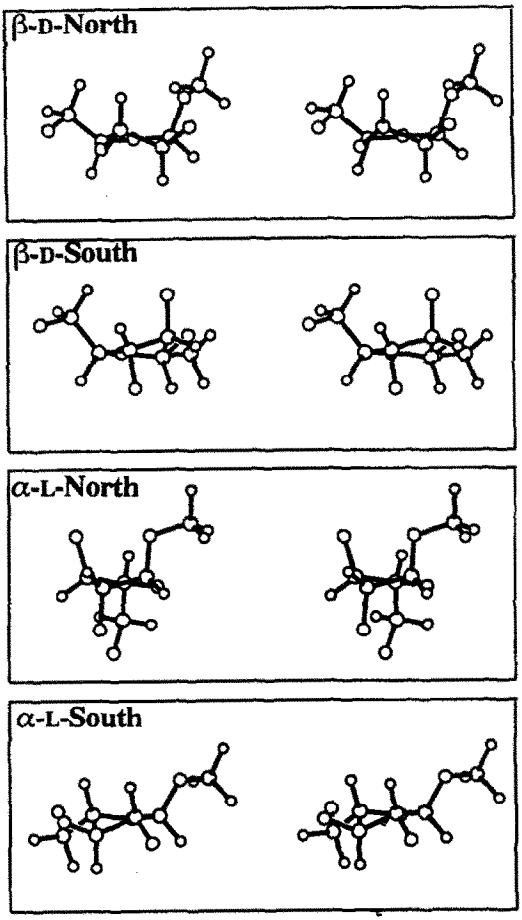


Fig. 5. Stereo drawings of North and South lower energy conformations for both β-D- and α-L-arabinofuranoside. The hydroxymethyl group is in its lowest energy orientation (*gt* for β-D- and *gg* for α-L-arabinofuranoside).

family pseudorotamers and South family pseudorotamers is more likely to occur via the East, i.e., the E_4 envelope, of the conformational wheel. These data can be compared to previous studies on five-membered ring conformations. Early *ab initio* works[7] demonstrated that cyclopentane undergoes almost free pseudorotation. When one of the methylene groups in cyclopentane is replaced by an oxygen atom (oxolane), the North and South conformations become favoured. Due to the two-fold symmetry of the molecule, the conformational pathways through the West and the East are equally probable[7]. Most conformational studies have been conducted on ribofuranose and 2-deoxy-D-erythro-pentofuranose ("2-deoxy-D-ribose"). Both molecules differ from β-D-arabinofuranose in their substitution at C-2. Energy calculations have been performed either by statistical studies based on the numerous crystal structures, classical molecular mechanics, consistent force-

field, semiempirical, and *ab initio* calculations[10]. All these data agree with a pseudorotational wheel very similar to the one computed for β-D-arabinofuranose (Fig. 4). The North and South family, usually respectively referred to as C-3(*endo*) (^3E) and C-2(*endo*) (E_2), are the two stable conformers. In this case also, the route of facile interconversion follows the pseudoration path through the East region ($^\phi E$). In both ribofuranose and β-D-arabinofuranose, the other route through E_ϕ [also called O-4(*exo*)] is unfavourable because this conformer has the axial orientation of both the CH_2OH group at C-4 and the substituent at C-1 (base or methyl) which are then in steric conflict.

These similarities between energy maps are not a general feature of all five-membered rings. The effect of substituents can greatly affect the conformational behaviour. Aldotetraoses such as threose and erythrose present very different behaviour[23]. Also, the molecular mechanics study on the ketohexose fructofuranose demonstrated that the North family is preferred over the South one[8,9].

Energy maps of the methyl α-L-arabinofuranoside ring.—Energy calculations were performed on methyl α-L-arabinofuranoside for the three orientations of the primary hydroxyl group *gg*, *gt*, and *tg*. The resulting pseudorotational energy maps are displayed in Fig. 6. Two main differences appear when comparing these maps with those of β-D-arabinofuranoside. First, the three orientations at C-4 generate quite different energy maps; second, when both the South and North family are present, the facile route is through the West (E_ϕ) region. The unfavoured conformation of the East region ($^\phi E$) can be explained by the occurrence of an unfavourable steric clash between the hydrogen at C-1 and the hydroxymethyl group at C-4 when both are in an axial orientation. The North and South conformations are equally populated for the *gg* orientation. The North conformer is not as favoured as in the β-D-arabinofuranose because of a steric interaction between the axial O-methyl group C-1 and the axial hydroxyl group at C-3. However, for the *gg* conformer an energy minimum exists due to the occurrence of an hydrogen bond between O-2 and O-5. Two conformers have been fully optimized and are displayed in Fig. 5. The α-L-North and α-L-South conformers have respective puckering parameters of (0.35, 236.7°) and (0.43, 117.4°).

The distribution of the exocyclic group conformations amongst the three stable staggered rotamers *gg*, *gt* and *tg*, (see Fig. 2) can be determined from the analysis of the vicinal coupling constants $^3J_{H4-H5R}$ and $^3J_{H4-H5S}$. These data were measured in low molecular fragments of arabinan[14]. Values of 3.4 Hz for the smallest coupling and 5.8 Hz for the larger one were obtained from the nonreducing unit of α-L-arabinofuranose (1 → 5)-α-L-arabinofuranose. These data are very similar to those measured on arabinoxylan oligosaccharides[13]. Solving the equations described in the Methods Section, indicates that assigning to the smallest value $^3J_{H4-H5R}$ would lead to a *gg* : *gt* : *tg* population of 45 : 51 : 4, which is in good agreement with data obtained on an arabinoxylan oligosaccharide[13].

In order to compare the calculated values with experimental values, the three intra-ring $^3J_{H-H}$ coupling constants were calculated for each conformation, and

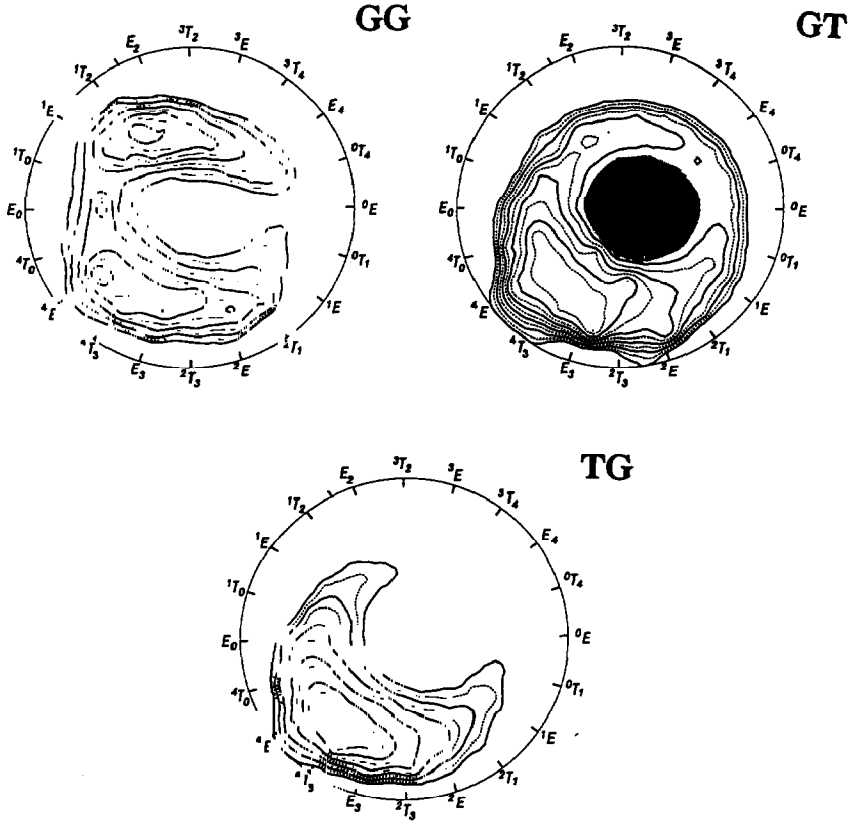


Fig. 6. Three pseudorotational energy maps of methyl α-L-arabinofuranoside corresponding to the three stable staggered orientations *gg*, *gt* and *tg*, of the exocyclic hydroxymethyl group. Isoenergy contours are drawn as in Fig. 4.

their isolines are reported as a function of the puckering parameters (Fig. 7). All the three coupling constants, $^3J_{H1-H2}$, $^3J_{H2-H3}$, and $^3J_{H3-H4}$, exhibit large variations due to the large amplitude of the ring torsion angle in the allowed range of pucker. For comparative purposes, the three intracyclic coupling constants calculated for the α-L-North and α-L-South low-energy conformers have been reported in Table I, along with the experimental values for both rings of (1 → 5)-α-L-arabinobiose[14]. The coupling constants of the nonreducing residue are very analogous to those obtained from the (1 → 3)-α-linked L-arabinose moiety of arabinoxylan[13]. None of the coupling constants calculated for the α-L-North conformer, nor those established for the α-L-South one, agree with the experimental values. The coupling constants were then averaged over all the pseudorotamers of each map according to the Boltzmann distribution. The averaging between the three rotamers *gg* : *gt* : *tg* was then conducted for the 45 : 51 : 4 population previously established. There is a good agreement between these averaged coupling constants and the experimental coupling constants measured at the reducing end of the arabinobiose. The results

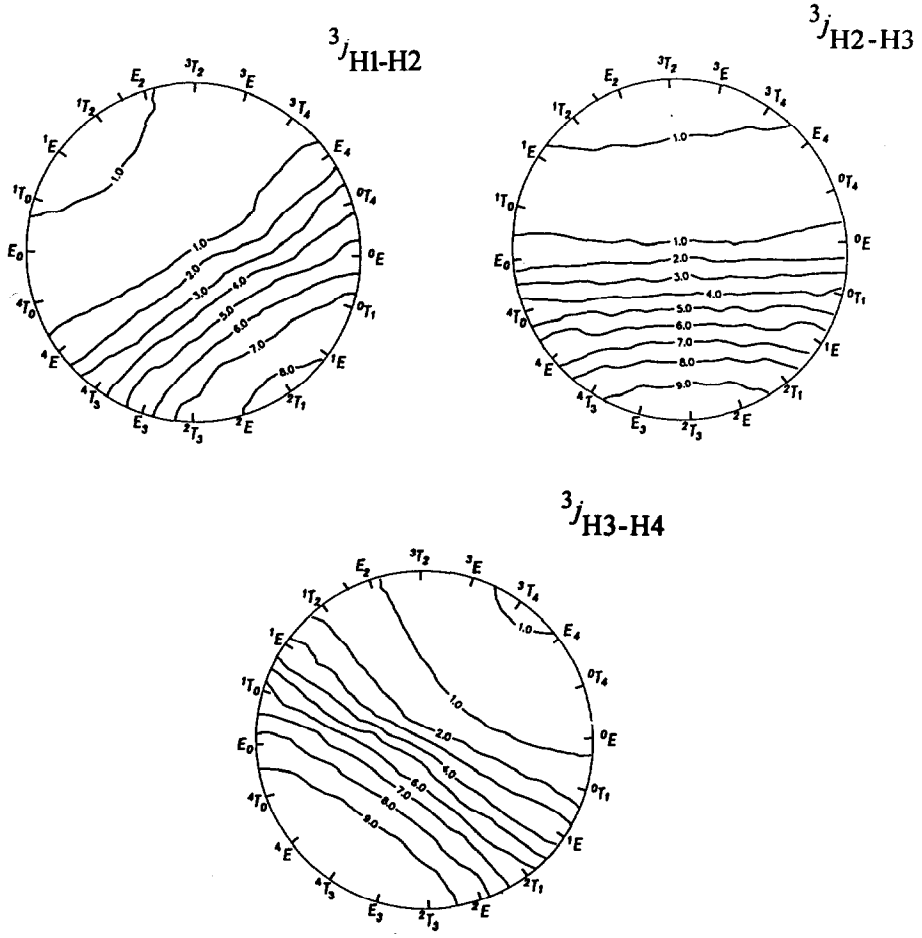


Fig. 7. Variations of the three intracyclic $^3J_{H-H}$ coupling constants as a function of the puckering parameters Q and ϕ.

TABLE I

Comparison of calculated and experimental intracyclic $^3J_{H-H}$ coupling constants (Hz) for methyl α-L-arabinofuranoside (2). The calculated averaged values take in account all the conformations of the energy maps with a proportion of 45:51:4 for the *gg / gt / tg* maps

Coupling constants	α-L-North minimum	α-L-South minimum	Averaged all conformations	Exp [a] Reducing	Exp [a] Nonreducing
$^3J_{H-1-H-2}$	1.3	4.6	3.1	3.6	1.7 [b]
$^3J_{H-2-H-3}$	0.8	9.3	5.2	6.0	3.2
$^3J_{H-3-H-4}$	1.7	9.5	7.4	7.0	5.8

[a] Obtained from spectral simulation on (1 → 5)-α-linked-D-arabinobiose[14] using the Bruker simulation package PANIC. [b] Measured on (1 → 5)-α-linked-D-arabinobiose.

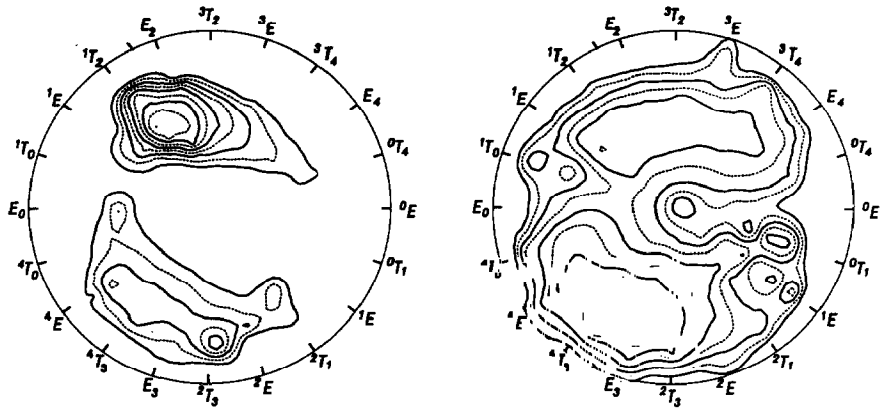


Fig. 8. Two pseudorotational energy maps of the reducing furanose ring of (1 → 5)-α-L-arabinobiose corresponding to two stable orientations of the ω torsion angle, *gg* and *gt*. Isoenergy contours are drawn by interpolation of 1 kcal/mol with respect to the absolute minimum.

indicate that the reducing end, which undergoes more flexibility, can span freely all the pseudorotational wheel.

Puckering map of the nonreducing residue in (1 → 5)-α-D-arabinobiose.—Finally the effect of substitution of another residue at O-1 on the furanose flexibility was considered. The energy pucker maps were established for α-L-arabinofuranose with another residue linked (1 → 5)-α-D. This substituent was selected successively in the possible North and South conformations, while the third torsion angle at the glycosidic linkage, ω was either *gg* or *gt*. Because of its low occurrence, the *tg* rotamer was not considered. These different calculations were represented as two "adiabatic" maps in Fig. 8, one for the *gg* orientation at the glycosidic linkage, and one for the *gt* orientation. When compared to the energy maps of Fig. 6, it appears that the substitution slightly reduces flexibility of the nonreducing furanose ring. However, in both cases, North and South conformations are still possible. However, interconversion between these two families is predicted to be more difficult in the case of the disaccharide.

CONCLUSIONS

The present work shows that the conformational behaviour of both methyl α-L- and methyl β-D-arabinofuranoside can be fully described using molecular mechanics calculations. Potential energy surfaces as a function of the two puckering parameters Q and φ can be established. As in the case of ribose, "2-deoxyribose" and fructofuranose, energy minima are observed in both the Northern and Southern zones. The preferred routes between the Northern and Southern minima can

be easily pictured. These maps suggest that there are substantial differences in the dynamically accessible conformations of the two molecules. The puckering parameters of low-energy regions agreed well with experimental ones, as 20 of the 22 available puckering values of β-D-arabinofuranose that have been observed in crystals are within 0.7 kcal/mol of the minimum. The outliers have energies up to only 1.7 kcal/mol above the minimum, an observation that may be well explained by crystal forces. As for the modeling of the solution behaviour of the α-L analogue, the agreement reached between the observed and the calculated data indicates that we have been able to calculate consistent energy maps for various puckering and various orientations of the primary hydroxyl groups. In the case of the α-L configuration, the effect of the substitution at O-1 by another arabinofuranose moiety slightly reduces the conformational flexibility of the nonreducing residue. Both the North and South conformers are still likely to occur, and only their interconversion is expected to be altered. All the structural features described in the present work will provide the basis for further investigations of the likely conformations of arabinofuranose containing molecules such as arabinans and arabinoxylans.

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