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Solution conformation of (1→4)-β-D-mannan from optical rotation

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ABSTRACT

Through the application of a recently developed calculational model of saccharide chiroptical properties, the optical rotation of (1→4)-β-D-mannan is calculated as a function of its linkage geometry in terms of φ(H-1–C 1–O-1–C-4′) and ψ(C-1–O-1–C-4′–H-4′). The experimental optical rotation indicates that the predominant linkage-conformation is in the region near $60° \leq \varphi \leq 80°$, $-20° \leq \psi \leq 20°$, in agreement with some, but not all, calculated potential-energy surfaces.

INTRODUCTION

(1→4)-β-D-Mannans are plant polysaccharides having both structural and energy-reserve functions[1,2]. Forms carrying other sugar units as side chains are common; galactomannans have commercial importance as gelling enhancers in mixed polysaccharide systems[3].

Solid-state structures have been established for mannobiose[O-β-D-mannopyranosyl-(1→4)-α-D-mannopyranose][4], mannotriose[5], and mannan I (ref. 6), one of two crystalline polymorphs. Their linkage geometries, expressed in terms of the dihedral angles φ(H-1–C-1–O-1–C-4′) and ψ(C-1–O-1–C-4′-H-4′) are similar, $25° \leq \varphi \leq 40°$, $-26° \leq \psi \leq -44°$. O-5–O-H-3′ hydrogen bonds are found in all.

Potential-energy φ,ψ maps have been calculated for the disaccharide[5,7–10] and for a mannan chain.[7] Calculated φ,ψ energy maps for the disaccharide[5,7–10] are generally similar to one another with respect to the appearance of three allowed regions (Fig. 1), as in other β-(1→4)-linked disaccharides (cellobiose and lactose). Calculated maps for mannobiose differ from one another, however, with respect to the number of local minima within the major region and with respect to the calculated global minimum-energy conformation. One calculated minimum-energy conformation is similar to the crystal conformation, $(\varphi,\psi) = (30°, -39°)$.[5] Three others similarly have O-1–C-4′ *gauche* to C-1–O-5, $(\varphi,\psi) = (47°, 20°)$[7], $(\varphi,\psi) = (47°, 0°)$[8], and $(\varphi,\psi) = (61°, -1°)$[10]. A fourth has O-1–C-4′ approximately eclipsing C-1–O-5, $(\varphi,\psi) = (112°, -29°)$[9]. The two most recent calculations have incorporated solvent in a continuum model[9,10].

We have been interested in establishing solution conformations of saccharides from optical rotation measurements, using a calculation model recently developed[11,12].

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Previous applications have been to cellobiose[12], maltose[12], lactose[13], trehalose[14], and the neutral pectic polysaccharide (1→4)-β-D galactan[15]. Our approach has been to combine an analysis of optical activity measurements with molecular-modeling calculations from the literature to generate a description of solution conformations consistent with both methods. In some cases (cellobiose[12], lactose[13] and galactan[15]) the observed optical rotation is consistent with published φ,ψ energy maps, with indications of flexibility about a well defined conformation. For trehalose, we found agreement with calculated φ,ψ maps that indicate very limited flexibility[14]. For maltose, optical rotation indicates a predominant conformation in aqueous solution that differs from the extended crystal conformation, a result consistent with some, but not all, molecular-modeling studies[12]. In this manner our model can play a role in guiding the development of force fields which lead to the *effective* potential-energy surface in water.

DISCUSSION

The calculational model has been described in detail in previous applications. Mannose ring-atom coordinates were adopted from the glucose geometry of Arnott and Scott[16]. Small variations in ring geometry, typical of those found in solid-state structure determinations of variously substituted pyranoses[16], affect the calculated optical rotation, but by an amount smaller than the overall uncertainty in the calculational model, which is estimated[12] to be ± 24 deg cm^2 dmol^{-1}. In the present case, for example, we calculate the rotation of monomeric β-D-mannose to be − 36 deg cm^2 dmol^{-1} using the Arnott–Scott coordinates[16], − 37 deg cm^2 dmol^{-1} with the mannose-ring coordinates observed in *N*-acetyl-β-D-mannosamine[17] and − 41 deg cm^2 dmol^{-1} for the mannose ring coordinates reported by Chanzy *et al.*[6] for mannan I, fixing the hydroxymethyl group in each case to be in the *gt* conformation, namely, *gauche* to O-5 and *trans* to C-4.

For oligomer calculations the glycosidic angle was taken to be 117°, and the hydroxymethyl group of each residue was examined in two conformations, *gg* and *gt*. The optical rotation of the disaccharide, averaged over the four resulting conformers, with a *gg/gt* ratio[18] of 0.33/0.67,[18] is given by

$$[M] = 0.11[M]_{gg,gg} + 0.22[M]_{gg,gt} + 0.22[M]_{gt,gg} + 0.44[M]_{gt,gt}$$

where $0.11 = (0.33)^2$, $0.22 = (0.33)(0.67)$ and $0.44 = (0.67)^2$. We found the approximation

$$[M]_{gg,gt} + [M]_{gt,gg} = [M]_{gg,gg} + [M]_{gt,gt}$$

to be accurate to within 4%, indicating that the contribution of the hydroxymethyl group to optical rotation is nearly independent of the hydroxymethyl group conformation on the neighboring residue. We therefore used the expressions:

$$[M]_{\text{dimer}} = 0.33[M]_{gg,gg} + 0.67[M]_{gt,gt}$$

$$[M]_{trimer} = 0.33[M]_{gg,gg,gg} + 0.67[M]_{gt,gt,gt}$$

We then calculated the molar-residue rotation of an internal residue of a (1→4)-β-D-mannan chain, $[M]_{polymer}$, in a nearest-neighbor approximation[15], as the difference between the trimer and dimer rotations, each calculated in a given linkage geometry. We tested the dependence of calculated results on the statistical weight ratio, *gg/gt*, of the hydroxymethyl group. With *gg/gt* = 0.50/0.50, the disaccharide and trisaccharide rotations are, on average, 19 and 30 deg cm^2 dmol^{-1} more negative, respectively; the calculated molar-residue rotations, $[M]_{polymer}$, are 11 deg cm^2 dmol^{-1} more negative.

Table I shows the results of the calculations. In Fig. 1 the molar residue rotations, $[M]_{polymer}$, are shown together with the energy contour 10 kcal mol^{-1} above the energy minimum, as calculated by Tvaroska *et al.*[9]. The molar-residue rotation of mannan I solubilized in aqueous sodium hydroxide has been reported[19] to be −75 deg cm^2 dmol^{-1}; another recent value[20] is −79 deg cm^2 dmol^{-1}. Dialysis against water[20] gives −69 deg cm^2 dmol^{-1}. The average incremental molar-residue rotation of manno-oligosaccharides in water is[20,21] −88 deg cm^2 dmol^{-1}.

The calculated rotations are relatively strongly dependent on linkage conformation (Fig. 1), and the only region of (φ,ψ)-space with conformations having rotations in the range of the observed values (−70 to −90 deg cm^2 dmol^{-1}) is the small region $60° \leq \varphi \leq 80°$ and $-20° \leq \psi \leq 20°$. In conformations within this region, O-1–C-4′ is *gauche* to C-1–O-5, as observed in crystal structures[4-6] and as occurs in the global energy-minimum conformation of several molecular-modeling studies.[5,7,8,10] That geometry is favored by the O-5–C-1–O-1–C-4′ torsional-energy contribution, including any exoanomeric effect that may be present; O-5–O-3′ interactions are also favorable. Our

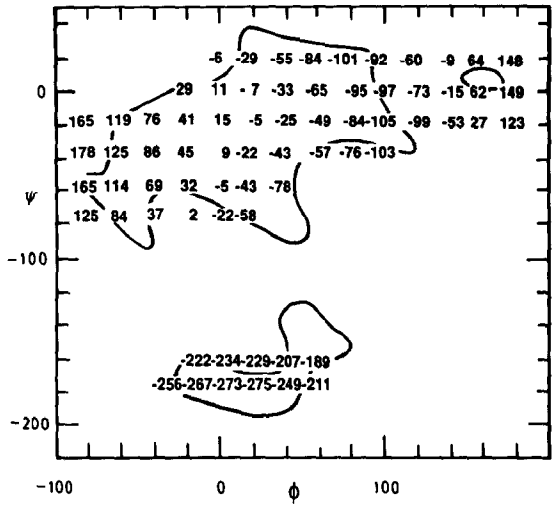

Fig. 1. Calculated molar-residue rotation, $[M]_{polymer}$, for an internal residue of a (1→4)-β-D-mannan chain, in units of deg cm^2 dmol^{-1}, together with the energy contour 10 kcal mol^{-1} above the calculated minimum of Tvaroska *et al.*[9]

TABLE I

Calculated molar rotation of β-mannobiose and β-mannotriose, and calculated molar-residue rotation of (1→4)-β-D-mannan as a function of linkage conformation, in units of deg cm^2 dmol^{-1}. $[M]^{obsd}_{polymer} = -75$

(φ,ψ)	$[M]_{dimer}$	$[M]_{trimer}$	$[M]_{polymer}$
(−80°, −20°)	47	212	165
(−80°, −40°)	56	234	178
(−80°, −60°)	51	216	165
(−80°, −80°)	25	150	125
(−60°, −20°)	14	133	119
(−60°, −40°)	16	141	125
(−60°, −60°)	3	117	114
(−60°, −80°)	−21	63	84
(−40°, −20°)	−18	58	76
(−40°, −40°)	−30	56	86
(−40°, −60°)	−48	21	69
(−40°, −80°)	−75	−38	37
(−20°,0°)	−41	−12	29
(−20°, −20°)	−51	−10	41
(−20°, −40°)	−71	−26	45
(−20°, −60°)	−99	−67	32
(−20°, −80°)	−131	−129	2
(0°,20°)	−54	−60	−6
(0°,0°)	−58	−47	11
(0°, −20°)	−76	−61	15
(0°, −40°)	−107	−98	9
(0°, −60°)	−144	−149	−5
(0°, −80°)	−183	−205	−22
(20°,20°)	−63	−92	−29
(20°,0°)	−67	−74	−7
(20°, −20°)	−91	−96	−5
(20°, −40°)	−131	−153	−22
(20°, −60°)	−178	−221	−43
(20°, −80°)	−224	−282	−58
(40°,20°)	−68	−123	−55
(40°,0°)	−68	−101	−33
(40°, −20°)	−91	−116	−25
(40°, −40°)	−136	−179	−43
(40°, −60°)	−194	−272	−78
(60°,20°)	−69	−153	−84
(60°,0°)	−65	−130	−65
(60°, −20°)	−80	−129	−49
(60°, −40°)	−120	−177	−57
(80°,20°)	−71	−172	−101
(80°,0°)	−57	−152	−95
(80°, −20°)	−63	−147	−84
(80°, −40°)	−95	−171	−76
(100°,20°)	−68	−160	−92
(100°,0°)	−51	−148	−97
(100°, −20°)	−49	−154	−105
(100°, −40°)	−67	−170	−103
(120°,20°)	−58	−118	−60
(120°,0°)	−37	−110	−73
(120°, −20°)	−35	−134	−99
(140°,20°)	−40	−49	−9

TABLE I (continued)

Calculated molar rotation of β-mannobiose and β-mannotriose, and calculated molar-residue rotation of (1→4)-β-D-mannan as a function of linkage conformation, in units of deg cm^2 dmol^{-1}. $[M]^{obsd}_{polymer} = -75$

(φ,ψ)	$[M]_{dimer}$	$[M]_{trimer}$	$[M]_{polymer}$
(140°,0°)	−16	−31	−15
(140°, −20°)	−11	−64	−53
(160°,20°)	−11	53	64
(160°,0°)	18	80	62
(160°, −20°)	28	55	27
(180°,20°)	18	166	148
(180°,0°)	52	201	149
(180°, −20°)	73	196	123
(−40°, −180°)	−199	−455	−256
(−20°, −160°)	−232	−454	−222
(−20°, −180°)	−234	−501	−267
(0°, −160°)	−274	−508	−234
(0°, −180°)	−271	−544	−273
(20°, −160°)	−313	−542	−229
(20°, −180°)	−302	−577	−275
(40°, −160°)	−348	−555	−207
(40°, −180°)	−330	−579	−249
(60°, −160°)	−375	−564	−189
(60°, −180°)	−354	−565	−211

analysis of optical rotation is thus consistent with molecular-modeling calculations that indicate this region of (φ,ψ)-space to be highly populated in aqueous solution.

Furthermore, our results indicate that the flexibility of the linkage geometry may be more restricted in water than indicated in some modeling studies. Large excursions within the major allowed region would lead to an average rotation much less negative than the observed value (Fig. 1). Although some population of 'folded' conformations near $\psi = 180°$ could compensate, the simpler interpretation of our results is that the effective potential-energy surface in aqueous solution is highly restrictive. Our recent results on (1→4)-β-D-galactan were similar[15]. Extensive dynamics calculations which include solvent molecules explicity may ultimately shed light on this matter.

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