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THE INFLUENCE OF SIDECHAINS ON THE CALCULATED DIMENSIONS OF THREE RELATED BACTERIAL POLYSACCHARIDES

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ABSTRACT

The effect of van der Waals interactions between sidechain and backbone on the shape of three bacterial polysaccharides in solution has been investigated. The three polymers, namely, gellan, welan, and rhamsan, share the same four-sugar backbone repeating-unit. Gellan is unbranched, whereas welan and rhamsan display comblike branching. Consequently, the effect of chain branching on backbone conformation may be investigated. Van der Waals repulsive interactions of sidechain and backbone serve to limit, somewhat, the range of conformational freedom of the welan backbone in comparison to that of gellan. Attractive sidechain–backbone interactions, which may be as significant as 2–3 kcal/mol, predominate over much of the accessible conformational space of the welan backbone. Despite the strength of these interactions, the unperturbed shape of welan in solution is calculated to be very similar to that of the unbranched gellan. Attractive sidechain–backbone interactions in rhamsan have a modest influence on the conformational characteristics of the rhamsan backbone. The calculated, unperturbed conformation in solution is slightly more extended than that of gellan and welan, but the fundamental shape of the chain is changed only slightly. Significant differences in the physical properties of these polymers seem not to arise from differences in their random-coil conformations provoked by van der Waals interactions of sidechain and backbone. Other contributions to the sidechain–backbone interaction, *e.g.*, hydrogen bonding, could be involved; interchain interactions are also likely to be important.

INTRODUCTION

The conformations of a number of relatively simple polysaccharides in solution have been treated quantitatively by using realistic, polymer-chain models and the statistical-mechanical theory of polymer-chain conformation[1–6]. In all instances, attention has heretofore been restricted to linear polysaccharides. Included among these are refined chain models for two linear, copolymeric species,

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pullulan[6] and a barley (1→3,1→4)-β-D-glucan[5]. Complex microbial polysaccharides have recently assumed a significant position among the industrially important, bulk and specialty polymers; dextran, schizophyllan, and xanthan are prominent cases in point. Usually the microbial polymers are regularly repeating copolymers which may contain up to eight sugar residues in the repeating unit[7] Often, these polymers display comblike branching, with as many as four sugar residues in the branch unit.

A general understanding of the role of these branches in determining the physical properties of the microbial polysaccharides has not yet been achieved. The branches frequently carry ionic charges, and are thus likely to be strongly involved in the intermolecular interactions, including the solvation, of the polymer The entropy of mixing that arises from their flexibility may, in some cases, help to promote the solubility of the chains. Finally, and most fundamentally, the side-chains may be involved with the polymer backbone in interactions that influence the conformational freedom of the backbone, and thus the shape of the chain in solution It is the latter effect that we have now explored by using a straightforward

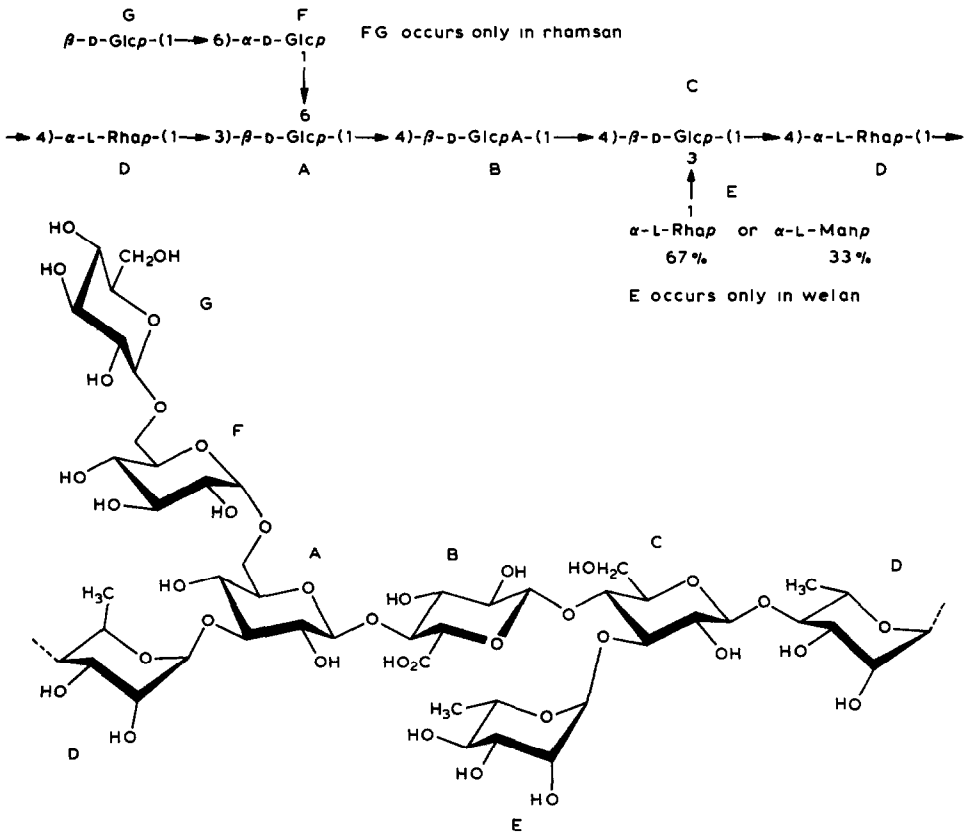

Fig 1 A schematic drawing of the chain segments considered [Segment ABCD represents the repeating unit of gellan This backbone repeating unit is substituted at residue C with residue E in welan, and at residue A with sidechain FG in rhamsan.]

elaboration of the aforementioned theoretical methods that have been useful in understanding the solution properties of many simpler polysaccharides.

For this study, we selected three bacterial polysaccharides differing only in their sidechain structures. All three, gellan, welan, and rhamsan, are commercial products of Kelco, Division of Merck. Gellan (formerly, PS-60) forms sturdy, clear gels at low concentration of the polymer, whereas welan (formerly, S-130) and rhamsan (formerly, S-194) are useful for their large increment in viscosity in aqueous solution[8,9]. The linear, four-sugar repeating-unit of gellan [→3)-β-D-Glc*p*-(1→4)-β-D-Glc*p*A-(1→4)-β-D-Glc*p*-(1→4)-α-L-Rha*p*-(1→] is common to the three polymers[9–13]. This unit is designated ABCD in Fig. 1. Welan bears a (1→3)-linked α-L-Rha*p* (67%) or α-L-Man*p* (33%) substituent on this backbone at sugar C. This substituent is shown as α-L-Rha*p* in Fig. 1, where it is labeled as sugar E. A two-sugar sidechain, β-D-Glc*p*-(1→6)-α-D-Glc*p*-(1→6)-, occurs in rhamsan on backbone sugar A. The sugars of the rhamsan sidechain are designated F and G in Fig. 1. All three polysaccharides, gellan, welan, and rhamsan, contain *O*-acetyl groups but, because their locations are currently unknown, these groups have been ignored in the present analysis. The structural relationships of these three polymers, which have quite different physical properties[8,9], provide an excellent arena in which to explore the influence of comblike branching in determining the properties of the complex, microbial polysaccharides.

THEORETICAL METHODS

Structural parameters. — It is assumed throughout that the sugar residues are rigidly constrained to their most stable chair conformations. Conformational variability of the polymers is thus allocated strictly to the torsional variables ϕ and ψ for rotations about the glycosidic and aglycon bonds, respectively, of the linkage region and to the torsional variable ω for rotations about the C-5–C-6 bond in the case of (1→6)-glycosidic linkages[14,15]. Glc*p* and Glc*p*A residue geometries were taken from the averaged parameters for α- and β-D-glucose recommended by Arnott and Scott[16]. The geometry of the α-L-Rha*p* residue was generated by "epimerization" of the appropriate atoms of the Arnott–Scott α-D-glucose[3], and the unit was placed in the $^1C_4$ form[17] in order to position the maximum number of hydroxyl groups having an equatorial orientation. Because refined polymer-chain models were not sought in the present work, the potential-energy functions chosen do not discriminate between CH_3, CH_2OH, and CO_2H on C-5. It was therefore unnecessary to provide a separate residue-geometry for the α-L-Man*p* residue, which occurs in one-third of the residues as the substituent group in welan. The geometry of the glycosidic linkages was based upon the work of Arnott and Scott[16], and the valence angle at the glycosidic oxygen atom was set invariably at 117°.

Conformational energies — Conformational-energy functions used to generate the conformational-energy surfaces considered herein have recently been described in detail[6]. In the present case, however, terms to describe contributions

from torsional strain, *i.e.*, the first five terms on the right-hand side of Eq. *3* of ref. 6, have been omitted, in keeping with earlier practice[18] The chain models here described are to be considered unrefined, in the sense that the geometry and potential function parameters have not been so adjusted as to bring the characteristics of the model into quantitative agreement with appropriate, observable properties of the several polymers[3–6,15].

In prior application of these potential-energy functions to linear-polysaccharide chains, it has usually been considered sufficient to take into account only the interactions of nearest-neighbor sugar residues in the chain sequence[3,4,14,15]. In dealing with branched polysaccharides, it is necessary, however, also to consider the interactions of residues that are not directly connected to one another by a glycosidic linkage. The evident possibility for an important interaction of residue B and E in the welan repeating unit (see Fig. 1) is an example of this requirement. Likewise, in the present case, we shall take into account the interactions of backbone residues, such as B and D, which are second-neighbors in the backbone sequence. Interactions of the latter sort are normally of minor significance[3,4,14,15], and remain so in this instance. They may, however, assume considerable importance when (1→2) linkages occur in the backbone, as they frequently do in complex microbial polysaccharides.

A complete description of our method for dealing with second-neighbor interactions, *i.e.*, those of residues separated by two glycosidic linkages, has been provided[19]. Here, only an outline of the method will be discussed. To describe the treatment of sidechain–backbone interactions, we focus attention, for example, on the effect of sidechain residue E in welan on the orientational freedom of the glycosidic linkage between backbone residues B and C. (Residue E might be suspected of having an effect on linkages CD and AB as well, but these effects are, in this case, readily shown to be minor compared to the influence of E on the linkage BC; space-filling molecular models suffice to clarify this point.) Initially, the first-neighbor interaction-energy of residues B and C is computed for every mutual orientation of residues B and C governed by the ϕ, ψ pair of the intervening linkage. Then, to this first-neighbor interaction-energy for each conformation of the BC dimer is added the mean energy of interaction of residues B and E, averaged over all values of the ϕ, ψ pair associated with the glycosidic linkage EC. This mean energy is clearly a function of the ϕ, ψ angles for the dimer BC The sum of the first-neighbor energy of B and C and the mean second-neighbor energy of B and E for each conformation of the dimer BC then constitutes a revised conformational-energy surface for the BC backbone dimer which incorporates, in an approximate way, the influence of the side group E on the flexibility of the backbone. (The energy of interaction of residue E with residue C, although substantial, is independent of the conformation of the dimer BC, and thus does not influence the conformational characteristics of the chain backbone.)

The second-neighbor interaction of backbone residues B and D is incorporated in similar fashion; that is, to the first neighbor energy-surface of residues A

and B is added the mean energy of the interaction of B and D, averaged over all values of the ϕ, ψ pair associated with the DA linkage In taking into account the second-neighbor interactions in the backbone, it is necessary to look in only one direction along the chain, in order to avoid double counting of the contributions; having taken into account the interaction of residue B with its second-neighbor D toward the nonreducing end of the chain it is not proper to consider also its interaction with second-neighbor residue D toward the reducing end.

Unperturbed chain properties. — The chain models developed here for gellan, welan, and rhamsan were used to calculate three properties of the unperturbed polymer chain, all of which reflect the mean spatial characteristics, *i.e.*, the shape[4,14,15] of the randomly coiling chain. The term "unperturbed" in this context implies a polymer chain whose conformational properties are determined entirely by interactions of short range in the chain sequence, *e.g.*, residue E with residue B as already described, and which is therefore free from perturbation from the long-range excluded-volume effect[4,20,21]. The conformational properties of interest here are: (*1*) the mean end-to-end or persistence vector $\langle \mathbf{r} \rangle_0$ and its magnitude $a = |\langle \mathbf{r} \rangle_0|$, which we call the persistence length of the chain; (*2*) the mean-square end-to-end length of the chain $\langle r^2 \rangle_0$ and, especially, the characteristic ratio $C_x = \langle r^2 \rangle_0 / xL^2$, which is this quantity normalized by the number (x) of sugar residues in the chain and the mean-square bond-length (L^2) of the residue vectors spanning these sugars; and (*3*) the correlation function, f_x, which is the mean projection of a unit vector oriented along the terminal-residue vector of the chain onto the direction of the initial-residue vector. Here, the subscript zero denotes the unperturbed conformation of the chain. These three properties and the procedures for calculating their values as a function of the backbone chain-length x have been discussed extensively[1,3,14]. It must be kept in mind that these are characteristics of randomly coiling polymer-chains in solution and reflect averages over the entire range of conformations accessible to the polymer chain, properly weighted according to the respective energies of these manifold conformations.

RESULTS AND DISCUSSION

Gellan. — Conformational-energy surfaces for the four linkages in the gellan backbone repeating-unit are shown in Figs. 2(a)–2(d). All four surfaces include a mean energy of interaction with a second-neighbor residue in the backbone, as described in detail in the legend to Fig. 2. The AB and BC maps (see Figs. 2a and 2b) are both for (1→4) linkages of β-D-Glc*p* (or β-D-Glc*p*A), and are, consequently, essentially identical; minor differences are attributable to differences in the second-neighbor interaction, as CH_2OH and CO_2H are not differentiated at this level of refinement. The map for the dimer CD is similar, inasmuch as the linkage is again of the equatorial–equatorial (*e–e*) type[4,22], but the details of the low-energy domain are different, and the position of the absolute minimum is shifted slightly, primarily because of changes in the positioning of the substituents

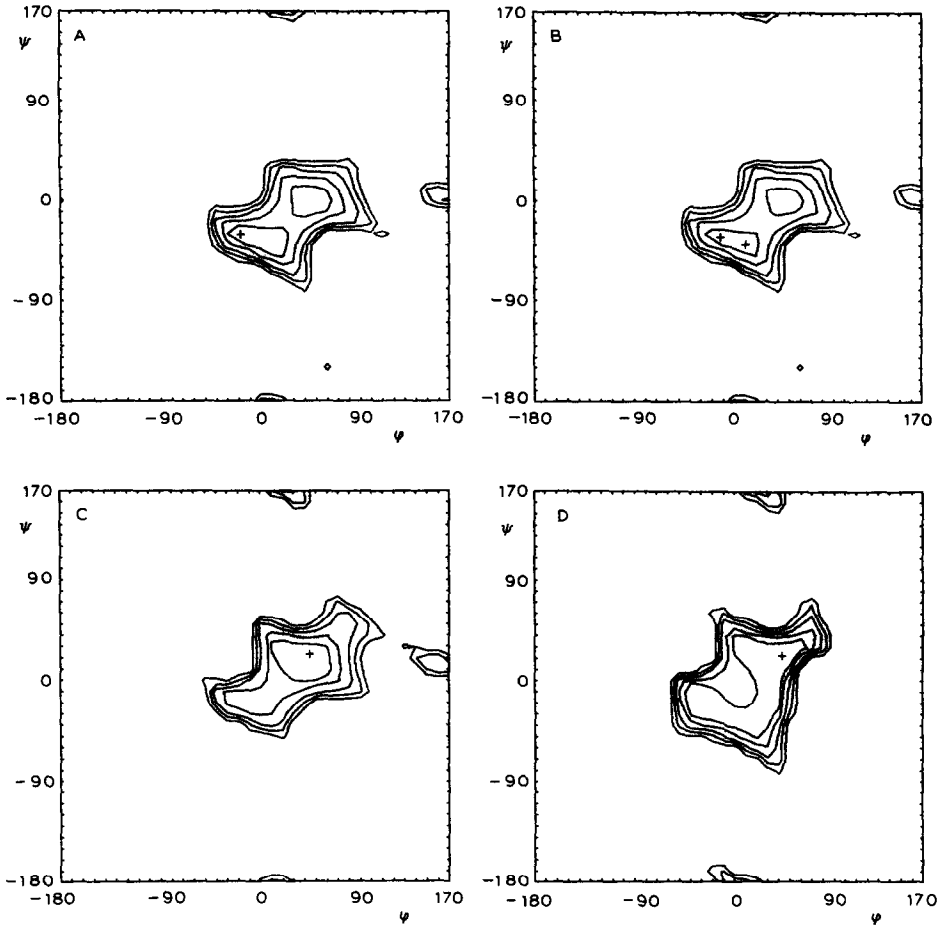

Fig 2 Conformational-energy contour-diagrams for gellan. [Energy minimum marked with + Lowest contour line, −1.0 kcal/mol. Successive contour lines at 0 0, 2 0, 4 0, and 6.0 kcal/mol. (a) Surface for AB dimer, including second-neighbor interaction of residue B with residue D toward nonreducing end of chain Minimum energy· −1.54 kcal/mol (b) Surface for BC dimer, including second-neighbor interaction of residue C with (nonreducing) residue A. Minimum energy. −1.34 kcal/mol. (c) Surface for CD dimer, including second-neighbor interaction of residue D with (nonreducing) residue B Minimum energy: −1 76 kcal/mol. (d) Surface for DA dimer, including second-neighbor interaction of residue A with (nonreducing) residue C Minimum energy· −2 22 kcal/mol.]

on ring D (α-L-Rha*p*) relative to the glycosidic linkage. The (1→4) *e–e* linkage is that found in cellulose, chitin, xanthan, and other highly extended, polysaccharide chains. As a point of reference, it is useful to observe that the homopolymeric β-D-glucan that is linked exclusively (1→4), *i.e.*, cellulose, is predicted, using energy surface AB or BC, to have a characteristic ratio C_∞ (at infinite chain-length) of ~100 and to generate highly extended, chain trajectories having strong directional persistence[3].

The fourth gellan energy-surface, for the dimer DA, corresponds to a (1→3)

axial–equatorial (*a–e*) linkage, and consequently has a shape different from that of the other three. Periodic incorporation of this linkage in the gellan backbone is expected to disrupt the pattern of nearly rectilinear chain-propagation enforced by the other three linkages[5], not only because the shape of the energy surface is different but especially because the geometry of the DA linkage serves to introduce a change in the direction of propagation of the chain[4]. This expectation is confirmed by the results of calculations of C_x for the gellan chain, given in Table I. The limiting value C_∞ at long chain-length is calculated to be 17.9. This is large by most standards[1–6] and connotes a highly extended chain conformation. The presence of the DA linkage has, however, diminished C_∞ to a value well below that calculated for the homopolymeric (1→4)-β-D-glucan.

The characteristic ratio C_x reflects the mean-square dimensions of the domain occupied by a single, randomly coiling chain[3]. Alternatively, the mean end-to-end or persistence vector of the chain, relative to a coordinate system rigidly attached to the chain origin[1], may be examined. This mean vector $\langle \mathbf{r} \rangle_0$ must converge to a limit with increase in chain length. As the chain becomes long enough, all memory of its original direction of propagation is lost at the chain terminus, and another unit added to the chain end displays random orientation relative to the molecule-fixed, coordinate system at the origin. It consequently makes no net contribution to the mean chain-extension measured by $\langle \mathbf{r} \rangle_0$. Projections of $\langle \mathbf{r} \rangle_0$ for the gellan chain into the *xy* and *yz* planes are shown in Figs. 3a and 3b; the components of $\langle \mathbf{r} \rangle_0$ and its magnitude, *a*, for infinite chain-length are given in Table II. The differences in ordinate and abscissa scales in Figs. 3a and 3b should be noted. All distances are in Ångström units, and each dot corresponds to a glycosidic oxygen atom, with the beginning of the chain placed at the origin of the coordinates. The mean displacement of each successive glycosidic oxygen atom from its predecessor clearly diminishes with increasing *x*, and the mean vector has sensibly converged after some 60 residues. It is clear that the mean extension of the gellan chain is mainly

TABLE I

CHARACTERISTIC RATIO AS A FUNCTION OF THE DEGREE OF POLYMERIZATION

Number of backbone residues (x)	*Gellan* C_x	*Welan* C_x	*Rhamsan* C_x
4	3 5	3 5	3 6
8	6 0	5 9	6 3
16	9 1	9 1	10 0
32	12 5	12 6	14 5
64	15 1	15 4	18 5
128	16 5	16 9	20 9
256	17 2	17 7	22 1
512	17 6	18 1	22 7
1024	17 8	18 3	23 0
2048	17 9	18 4	23 1
4096	17 9	18 5	23 2

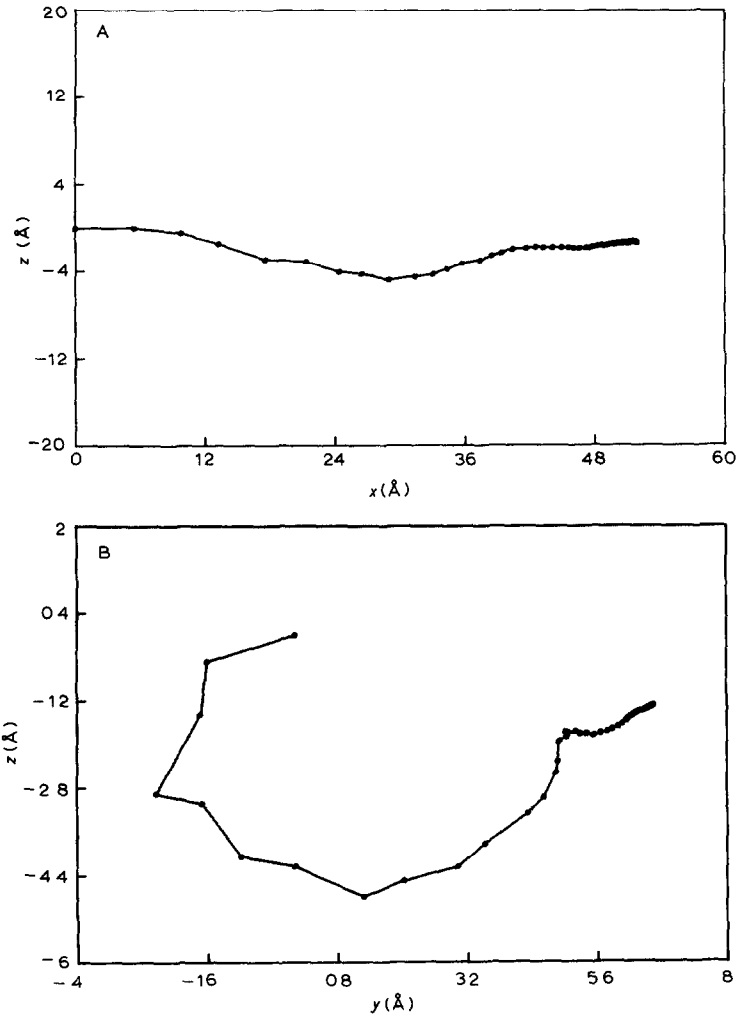

Fig 3 (a) Projection into the xz plane of the persistence vector $\langle \mathbf{r} \rangle_0$ for gellan. [Scale measured in Ångstrom units from origin at beginning of chain Black dots correspond to glycosidic oxygen atoms.] (b) Projection of $\langle \mathbf{r} \rangle_0$ for gellan into the yz plane

along the x direction, which corresponds to the O-1 to O-4 residue vector spanning a residue of type B, chosen arbitrarily to serve as the initial residue of the chain.

The convergence of the persistence vector is represented alternatively by the correlation function f_x, which describes the propensity of the chain to propagate in its original direction[3]. This quantity is plotted *vs.* chain length x for gellan in Fig. 4. The chain loses all memory of the original direction after ~60 residues, beyond which, f_x is indistinguishable from zero. A periodicity in the decay of f_x becomes evident after ~10 residues. At residue 13, a small peak appears, and this is repeated at every fourth residue thereafter. This periodicity, which certainly is closely related

TABLE II

PERSISTENCE VECTOR AT INFINITE CHAIN-LENGTH

Polysaccharide	*x Component* $\langle x \rangle$ *(in Å)*	*y Component* $\langle y \rangle$ *(in Å)*	*z Component* $\langle z \rangle$ *(in Å)*	*Magnitude* a *(in Å)*
Gellan	52 1	6 7	−1 3	52.6
Welan	53 6	5 8	−0 4	53 9
Rhamsan	64 6	6 3	10 2	65 7

to the four-sugar-backbone repeating-unit, reflects a small periodic tendency for the chain to regain its original direction of propagation, and thus, it signifies a small tendency to propagate with a helical trajectory.

Welan. — Substituent residue E, which occurs at backbone residue C in welan, only has a significant influence on backbone conformational freedom at linkage BC. An effect at linkage CD is perceptible, but it is too small to warrant reproduction of the energy surface; generally favorable interactions between residues E and D serve to increase the depth of the principal energy minimum by <0.1 kcal/mol in comparison to Fig. 2c. The BC energy-surface for welan is shown in Fig. 5. This surface includes, in addition to the first-neighbor interactions of residues B and C, and the (small) mean, second-neigbor interaction of residue C with residue A toward the nonreducing end of the chain, which was included in Fig. 2b, the mean energy of interaction of residue B with residue E, calculated as already explicitly described.

Two predominant effects of the interactions of sidechain residue E with

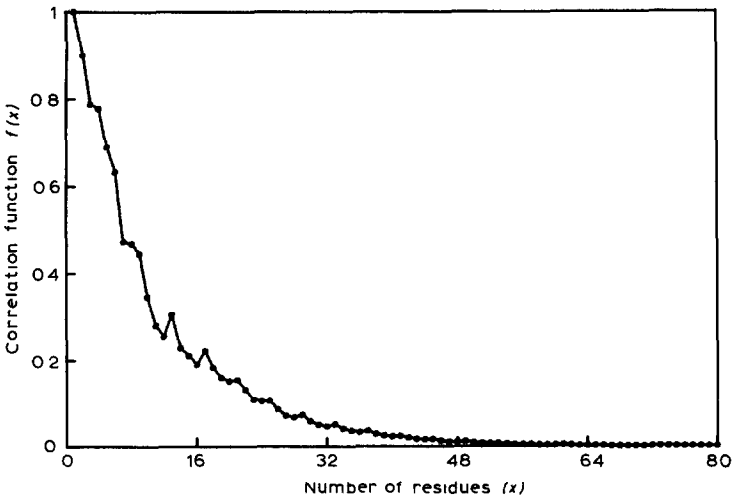

Fig. 4 Correlation function f_x for gellan plotted *vs* number of backbone residues (x). [The initial residue of the chain is chosen as residue B (β-D-Glc*p*A)]

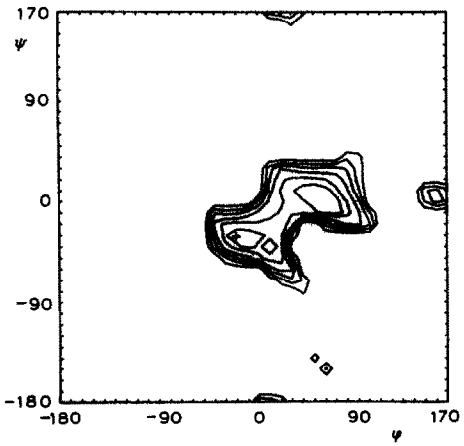

Fig. 5. Conformational-energy contour-diagram for welan BC dimer, including second-neighbor interaction of residue C with (nonreducing) residue A and second-neighbor interaction of residue B with substituent E. [Lowest contour line, −3.0 kcal/mol. Successive contour lines at −2.0, 0 0, 2.0, 4.0, and 6.0 kcal/mol Minimum energy at +· −3.82 kcal/mol.]

backbone residue B can be ascertained by comparison of Fig. 5 with Fig. 2b. First, the boundary in ϕ, ψ space of the domain of energetically accessible conformations has been crowded in the vicinity of the position $\phi = 40°$, $\psi = -30°$. This is simply an expression of the expected steric intrusion of sidechain residue E into the conformational space otherwise energetically allowed to the BC dimer. Less readily anticipated and, hence, more interesting, is the sharp diminution in the general level of energies in the allowed region of Fig. 5, where energies average at least 2 kcal/mol more negative than in the same region of Fig. 2b. This second effect discloses that, throughout most of the energetically allowed domain in the conformational space of the BC dimer, the mean interactions of the sidechain residue E with the backbone residue B (averaged over the conformational space of the EC dimer) are favorable; that is, E is so positioned relative to B as to engender, on average, many attractive van der Waals (and electrostatic) interactions between the two residues which are not compensated for by opposing van der Waals repulsions. That this interaction is attributed here primarily to van der Waals interactions (rather than hydrogen bonding or solvation effects) reflects the nature of the potential functions used, which do not include terms to mimic hydrogen-bonded interactions and which account for solvation effects in only a very nonspecific way[6,15]. Intramolecular hydrogen-bonding, the energetics of which are not currently known for carbohydrates in aqueous media, could, for example, contribute additional favorable interactions of residues E and B of 1 kcal/mol, or more. (The mean interactions of residue E with residue C could also be added to the BC energy-surface. They would make a significant negative contribution, but, being independent of ϕ and ψ for the BC dimer, as already pointed out, would not affect the shape of the surface.)

Despite the substantial contribution of the sidechain–backbone interaction to the energy surface BC of welan, when this surface (see Fig. 5) is taken in conjunction with the slightly revised CD surface and the unmodified AB and DA surfaces in order to calculate the properties of the unperturbed chain, neither the characteristic ratio nor the persistence vector is predicted to differ significantly from those for gellan (see Tables I and II). Plots of the persistence vector and correlation function of welan are likewise nearly indistinguishable from the respective plots for gellan in Figs. 3 and 4. Insensitivity of the predicted chain conformation of welan to the presence of the substituent sugar is readily understood. The shapes and locations of the least energetic domains of the energy surfaces in Figs. 2b and 5 are virtually the same. Thus, the probability distribution of BC dimer conformations is almost identical in gellan and welan, and the calculated chain properties are the same. It may be concluded that the substantial differences in physical properties between gellan and welan[8,9] cannot be explained on the basis of effects on the random-coil chain conformation arising from van der Waals interactions of the welan sidechain with the backbone.

Rhamsan. — In rhamsan, the gellan backbone is substituted at residue A by the two-sugar sidechain GF. Only the interactions of the proximal sidechain residue F with the main chain are considered at the present level of approximation. The mean interactions of residue F with residue D (averaged over the ϕ,ψ,ω conformational space of the FA dimer) have only a minor influence on the conformational-energy surface for the dimer DA. Low-energy regions of the DA surface for gellan (see Fig. 2d) are perturbed by perhaps -0.2 kcal/mol by the generally favorable interactions of residues F and D, but the shape of the surface is not otherwise perceptibly changed.

Effects of the mean interaction of residue F with residue B are more pronounced on the conformational-energy surface of the main-chain dimer AB. Here, the low-energy regions of the AB surface characteristic of gellan (see Fig. 2a) are lowered in general by >1 kcal/mol, and the position of the absolute minimum is shifted from $\phi = -20°$, $\psi = -30°$ to $\phi = 60°$, $\psi = 0°$. Nevertheless, the general outlines of the allowed-energy domain in Fig. 2a are not noticeably distorted by inclusion of the averaged interaction of residues F and B. When this surface is used with the revised DA surface and the original (gellan) BC and CD surfaces in order to compute the conformation-dependent properties C_∞, $\langle \mathbf{r} \rangle_0$, and a, a chain conformation somewhat more extended than those of gellan and welan is predicted (see Tables I and II).

This calculated increase in C_∞ and a, due essentially to perturbation of the AB conformational surface by sidechain–backbone interactions, can be understood qualitatively as follows. If each of the dimers BC, CD, and DA is fixed in its most probable conformation (marked by the + signs in Figs. 2b, 2c, and 2d, respectively), it may be shown that the rigid, helical-chain trajectory produced by confining the dimer AB to its minimum-energy position in Fig. 2a ($\phi, \psi = -20°, -30°$) has a much smaller axial translation per backbone repeating unit than if that dimer

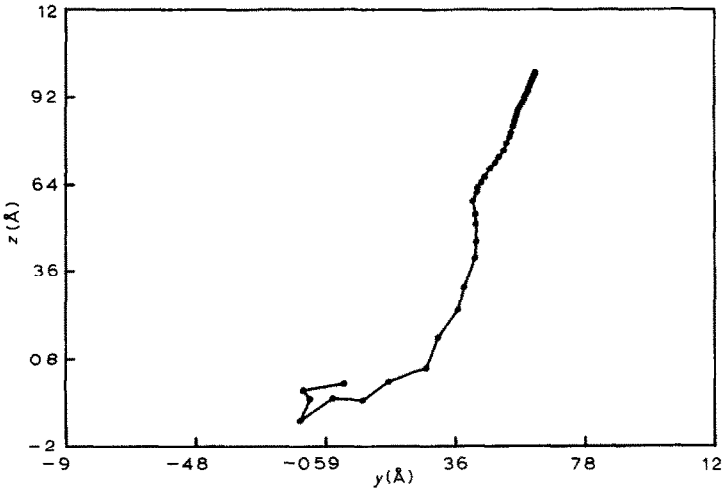

Fig. 6. Same as Fig 3b, but for rhamsan

is instead confined to the new minimum-energy position (ϕ, ψ = 60°, 0°) produced by the sidechain–backbone interaction in rhamsan. Although an argument based on the rigid, helical form may not always be reliable when applied to the random coil, we consider that, in this instance, it provides a reasonable picture of how the sidechain contribution to the backbone conformational properties of rhamsan works to extend the rhamsan chain conformation relative to that of gellan.

Aside from its greater extension in the x direction (see Table II), a projection of $\langle \mathbf{r} \rangle_0$ for rhamsan into the xz plane is rather similar to that for gellan in Fig. 3a. It does, however, traverse a somewhat larger range in the z dimension, and more monotonically, as shown by the yz projection in Fig. 6, which should be compared with Fig. 3b for gellan. The correlation function for rhamsan decays a little more slowly than for gellan, as expected for the more extended chain[3], and does not decline to zero until $x = \sim 80$. Otherwise, it is similar to that for gellan in Fig. 4, and shows the same fourfold periodicity. It is evident that, just as for the welan chain, the van der Waals interactions of the proximal residue of the rhamsan sidechain with its backbone do not perturb the random coil conformation much from that of its unbranched prototype, gellan.

CONCLUSION

Calculations involving three microbial polysaccharides, possessing the same four-sugar, backbone repeating-unit and differing only in that two of the three display comblike branching, show that the van der Waals interactions of the proximal sidechain residue with the backbone in the two branched polymers serve to alter only slightly the random-coil conformation of the unbranched polymer. In the systems studied, steric intrusion of the sidechain sugars into the conformational

space otherwise available to the backbone is of limited importance. Throughout most of the allowed conformational space of the backbone residues, they experience generally favorable interactions with residues of the nearby sidechains. These favorable interactions can be sufficient in magnitude, *i.e.*, averaging 2–3 kcal/mol in some cases, to have a significant influence on the effective conformational characteristics of the backbone. Repulsive sidechain–backbone interactions could, of course, be expected to exert a large influence as well, but they did not appear in the systems investigated here. A somewhat larger influence of sidechain–backbone, van der Waals interactions on the backbone trajectory was predicted to occur among certain *Klebsiella* polysaccharides[23].

The present calculations have considered only the van der Waals interactions of the sidechain and backbone. Contributions to the sidechain–backbone interactions from intramolecular hydrogen-bonding and specific solvation-effects are potentially significant. We have also ignored the negative charge of the carboxyl group, which occurs on every fourth backbone residue, the distal D-glucose residue on the rhamsan sidechain, and the *O*-acetyl substituents, the locations of which are still unknown. Of these approximations, the last is potentially the most significant, as shown by recent calculations on xanthan[24]; the carboxyl groups are spaced some 20 Å apart and would not interact strongly in aqueous media at modest ionic strength. Despite the approximations inherent in the present calculations, we consider that they suggest that the considerable differences in physical properties of gellan, welan, and rhamsan do not arise from sidechain-induced differences in the random-coil conformations of these polymers but, probably, from the effects of interchain interaction.

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REFERENCES

1 R. C JORDAN, D. A BRANT, AND A. CESÀRO, *Biopolymers*, 17 (1978) 2617–2632.
2 D A BRANT, *Carbohydr Polym*, 2 (1982) 232–237.
3 B A BURTON AND D A BRANT, *Biopolymers*, 22 (1983) 1769–1792.
4 D A BRANT, in J PREISS (Ed), *The Biochemistry of Plants*, Vol 3, Academic Press, New York, 1980, pp 425–472
5 G S BULIGA, D. A BRANT, AND G B FINCHER, *Carbohydr. Res*, 157 (1986) 139–156
6 G S BULIGA AND D A BRANT, *Int J Biol. Macromol.*, in press.
7 L KENNE AND B LINDBERG, in G ASPINALL (Ed.), *The Polysaccharides*, Vol 2, Academic Press, New York, 1983, pp. 287–363
8 V CRESCENZI, M DENTINI, AND I. C M. DEA, *Carbohydr Res.*, 160 (1987) 283–302
9 G T VEEDER AND K S KANG, *Symp. Biotechnol Microbial Polysacch.*, ACS Division of Microbial and Biochemical Technology, ACS National Meeting, Chicago, September, 1985

10 M A O'NEILL, R R SELVENDRAN, AND V J MORRIS, *Carbohydr Res*, 124 (1983) 123–133
11 P -E JANSSON, B. LINDBERG, AND P A SANDFORD, *Carbohydr. Res.*, 124 (1983) 135–139
12 P -E JANSSON, B LINDBERG, G WIDMALM, AND P A SANDFORD, *Carbohydr Res*, 139 (1985) 217–223
13 P -E JANSSON, B LINDBERG, J LINDBERG, E MAEKAWA, AND P A. SANDFORD, *Carbohydr Res*, 156 (1976) 157–163.
14 D A BRANT AND K D GOEBEL, *Macromolecules*, 8 (1975) 522–530.
15 D A. BRANT, *Q Rev Biophys*, 9 (1976) 527–596
16 S ARNOTT AND W E SCOTT, *J Chem Soc, Perkin Trans 2*, (1972) 324–335.
17 J F STODDART, *Stereochemistry of Carbohydrates*, Wiley–Interscience, New York, 1971.
18 C V GOEBEL, W L DIMPFL, AND D A BRANT, *Macromolecules*, 3 (1970) 644–654
19 T A TALASHEK AND D A BRANT, unpublished results
20 P J FLORY, *Principles of Polymer Chemistry*, Cornell Univ Press, Ithaca, New York, 1953
21 P J FLORY, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York, 1969
22 D. A. BRANT AND G S BULIGA, in R R COLWELL, E. R PARISER, AND A J SINSKEY (Eds), *Biotechnology of Marine Polysaccharides*, Hemisphere, New York, 1985, pp. 29–73
23 D A. BRANT AND T A TALASHEK, in V CRESCENZI, I. C. M. DEA, AND S S STIVALA, (Eds), *Recent Developments in Industrial Polysaccharides The Impact of Biotechnology and Advanced Methodologies*, Gordon and Breach, New York, 1987, in press
24 S PÉREZ AND C VERGELATI, *Int J Biol Macromol.*, in press