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Configurational Statistics of C(4)–C(8) Linked Homopolymers of (+)-Catechin or (−)-Epicatechin

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ABSTRACT: Configuration-dependent physical properties of homopolymers of (+)-catechin and (−)-epicatechin, linked from C(4) of one monomer to C(8) of the next, have been investigated by using rotational isomeric state theory. The characteristic ratios and components of the persistence vector have been evaluated for these polymers using structural information obtained from MM2 calculations for dimers of (+)-catechin and (−)-epicatechin. There are two rotational isomers at the interflavan bond between monomer units. Helices are formed if one rotational isomer is populated to the exclusion of the other. The chirality of the helix is determined solely by the selection of the rotational isomer. It is independent of the stereochemistry at C(3) and C(4). The polymers form random coils with unperturbed dimensions smaller than those of atactic polystyrene with the same molecular weight if the relative population of the two rotational isomers is assigned in the manner required by recent time-resolved fluorescence measurements and the rotational isomers are randomly distributed along the chain.

Polymers of (+)-catechin and (−)-epicatechin are abundant in the plant kingdom.[1–4] The structure of the monomers and the numbering scheme for atoms in the fused ring system are depicted in Figure 1. The older literature refers to these polymers as condensed tannins. The structure of (−)-epicatechin has been firmly established by X-ray crystallography.[5,6] In contrast, the free phenol form of (+)-catechin has thus far resisted crystallization in a form suitable for a structure determination. Nevertheless, the combination of crystal structures for several derivatives of (+)-catechin and (−)-epicatechin,[7–11] detailed analysis of coupling constants measured by high-resolution NMR,[11] theoretical conformational analysis,[12,13] and time-resolved fluorescence[14–16] has produced a good picture of the conformational behavior of the monomers and several dimers. This information provides an adequate basis for the construction of a realistic rotational isomeric state treatment of the higher polymers and a determination of the relationship between the conformational properties of a long chain and the type of linkage used for connection of the monomers.

The development of a realistic rotational isomeric state model for these polymers is a matter of some urgency because their conformational behavior in solution is controversial. The most common linkage is from C(4) of one monomer to C(8) of its neighbor.[17,18] Haslam[1] suggested that polymers with this type of linkage would form helices. Furthermore, the handedness of the helix was believed to be determined by the stereochemistry at C(3). The helices would be right-handed if the monomer units were (+)-catechin and left-handed if the polymer was formed from (−)-epicatechin.[1] Minimization of the conformational energy has been used for identification of helices of low energy for several types of oligomers.[19]

Two lines of experimental evidence are not easily reconciled with the proposition that the polymers are helical or rodlike. The overall dimensions, as measured by the behavior of peracetylated polymers upon gel permeation chromatography, are more compact than polystyrene of the same molecular weight.[2] Furthermore, there are two rotational isomers at the interflavan bond, and both rotational isomers are populated to a significant extent at ambient temperature in the free phenol forms of 4–6 and 4–8 linked dimers.[15,16] Interconversion of these rotational isomers is fast on the NMR time scale, but it is slow on the fluorescence time scale. A helix would be formed if one rotational isomer were populated to the exclusion of the other, but population of both rotational isomers should disrupt the helix and produce a random coil.

A rotational isomeric state model is described here for $4\alpha \rightarrow 8$ and $4\beta \rightarrow 8$ linked homopolymers of (+)-catechin and (−)-epicatechin. The required geometry and heterocyclic ring conformations used in the present analysis are based on MM2 calculations for the monomers[11] and dimers.[12,13] The MM2 algorithm provides excellent agreement with the crystal structure conformation of (+)-catechin–($4\alpha \rightarrow 2$)-phloroglucinol heptamethyl ether,[11] and also correctly predicts the preferred conformation of free (−)-epicatechin, as determined by the crystal structure. In this crystal structure (as well as in most other derivatives), the dihydroxyphenyl substituent at C(2) is placed in a pseudoequatorial position. An exception is provided by the crystal structure of penta-*O*-acetyl-(+)-catechin, where a pseudoaxial orientation is observed,[8] but MM2 calculation predicts a pseudoequatorial orientation.[11] This unusual conformation may arise from crystal packing forces (of intermolecular origin) not considered in the MM2 algorithm. Support for this contention is provided by the observation that the NMR coupling constants measured in solution are incompatible with the conformation adopted by penta-*O*-acetyl-(+)-catechin in the crystalline state.[11] Conformational analysis of the dimers of (+)-catechin and (−)-epicatechin using the MM2 algorithm has been performed for both axial and equatorial orientation of the C(2) substituent.[12,13] However, since the equatorial conformers are more frequently observed in solution[11] and

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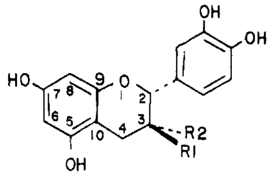

Figure 1. Structures of (+)-catechin (R1 = OH, R2 = H) and (–)-epicatechin (R1 = H, R2 = OH).

Table I
Parameters for 4 → 8 Linked Homopolymers

bond	monomer	linkage	length, Å	θ, deg	ϕ,[a] deg
1	either	α	1.40	62	180
	either	β	1.40	62	180
2	either	α	1.40	60	180
	either	β	1.40	60	–179
3	either	α	1.52	66	–135, –125
	either	β	1.51	66	114, 114
4	catechin	α	1.53	61	–134, 48
	epicatechin	α	1.53	61	–144, 39
	catechin	β	1.53	60	–35, 144
	epicatechin	β	1.53	60	–29, 154
5	either	α	1.41	60	179
	either	β	1.41	61	180
6	either	α	1.40	60	180
	either	β	1.40	60	–179
n	either	α	1.51		
	either	β	1.51		

[a] Dihedral angles are in the convention where $\phi = 0$ for a cis placement. Two dihedral angles are given for those bonds affected by the rotational isomerism at the interflavan bond.

are predicted to be more stable,[13] attention here is confined to the equatorial conformers.

Methods

Figure 2 depicts the sequence of bonds involved in the construction of the rotational isomeric state treatment for C(4)–C(8) linked homopolymers of (+)-catechin or (–)-epicatechin. The chain begins at the free C(8) at one end and terminates at the free C(4) at the other end. A polymer of x monomer units has $4x - 1$ bonds in this chain. Generator matrices appropriate for the homopolymers considered here are constructed in the manner described by Flory.[20]

The end-to-end vector, $\boldsymbol{r}_x$, for a chain with a specified degree of polymerization can be formulated in terms of the generator matrix, $\mathbf{A}_i$,

$$\mathbf{A}_i = \begin{bmatrix} \mathbf{T} & \boldsymbol{l} \\ 0 & 1 \end{bmatrix}_i \tag{1}$$

where the subscript denotes bond i in the chain. In eq 1, $\mathbf{T}$ specifies the matrix that transforms the components of bond $i + 1$, expressed in its own frame of reference, into the coordinate system of bond i, and $\boldsymbol{l}_i$ is the bond vector, l_i being the length of bond i.

The two rotational isomers for a dimeric unit will be called the *positive rotamer* and the *negative rotamer* (identifying the sign of the linkage torsion for the bond sequence shown in Figure 2). The formulation below is stated in terms of the probability for occupation of the rotamer at the interflavan bond (bond 4 in Table I) for which the dihedral angle is positive. The rotations about successive interflavan bonds are assumed to be independent, in view of the separation of monomer units $k - 1$ and $k + 1$ imposed by the fused ring system in monomer k. When $x > 1$, the expression for the end-to-end vector is

$$\boldsymbol{r}_x = \mathbf{A}_{[1}\boldsymbol{A}_2(\mathbf{F}_3\mathbf{F}_4\mathbf{A}_5\mathbf{A}_6)^{(x-1)}\mathbf{A}_{n]} \tag{2}$$

$$\mathbf{F}_3 = [f\mathbf{A}_3^{+}, (1 - f)\mathbf{A}_3^{-}] \tag{3}$$

$$\mathbf{F}_4 = \mathrm{col}\ (\mathbf{A}_4^{+}, \mathbf{A}_4^{-}) \tag{4}$$

and $\mathbf{A}_{[1}$ and $\mathbf{A}_{n]}$ denote the first three rows and last column of $\mathbf{A}_i$, respectively. The geometry used in each matrix is given in Table I. Inclusion of two different generator matrices for each of bonds 3 and 4 is imperative because of the differences in bond angles and dihedral angles at bonds 3 and 4 in the two rotamers. The interdependence of the pucker of the heterocyclic ring and the rotational isomer occupied at the interflavan bond causes the interdependence of $\mathbf{A}_3$ and $\mathbf{A}_4$. The last bond is bond n, and for a dimer, $n = 7$. Similar expressions can be used for evaluation of the mean-squared unperturbed end-to-end distance, $\langle r^2 \rangle_{x,0}$, with a change in the expression for the generator matrices.

$$\mathbf{A}_i = \begin{bmatrix} 1 & 2\boldsymbol{l}^T\mathbf{T} & l^2 \\ 0 & \mathbf{T} & \boldsymbol{l} \\ 0 & \mathbf{0} & 1 \end{bmatrix}_i \tag{5}$$

Here $\mathbf{A}_{[1}$ denotes the first row of $\mathbf{A}_1$.

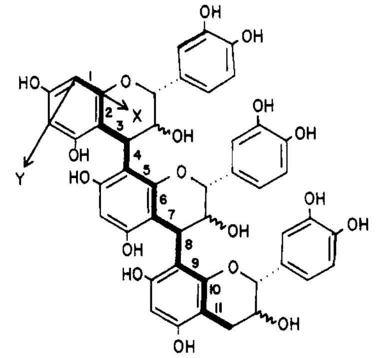

Figure 2. Sequence of bonds involved in the construction of the rotational isomeric state model. The numbers indicate the order of the bonds included in the treatment. The 2-fold rotational isomerism is around the interflavan bonds (bonds 4 and 8).

Unperturbed Dimensions

Molecular mechanics (MM2) calculations have shown that C(4)–C(6) linked and C(4)–C(8) linked dimers exhibit 2-fold rotational minima. The differences in energies at the minima are sufficiently small so that one rotamer will not necessarily dominate the other. MM2 calculations cannot determine the energy differences between the rotamers with sufficient accuracy for a precise specification of the value of f. Therefore, the initial step here is an examination of the configuration-dependent physical properties as a continuous function of the ratio of two rotamers. An appeal to the results of recent experimental work[15,16] will then define the relative population of the rotamers that is of particular interest.

Table II presents limiting values of characteristic ratios calculated for six different fractions of the positive rotamer. The characteristic ratio is defined as $\langle r^2 \rangle_0 / \sum l_i^2$. Of course, C is infinite when f is 0 or 1 because the end-to-end distance of the rigid helices is proportional to n. The smallest

Table II
Limiting Values of *C* for Different Fractions of the Positive Rotamer

		f					
monomer	linkage	0.1	0.2	0.4	0.5	0.8	0.9
(+)-catechin	$4\alpha \to 8$	79.8	35.0	16.4	13.8	53.5	58.4
(–)-epicatechin	$4\alpha \to 8$	69.0	31.5	15.3	14.0	64.0	66.5
(+)-catechin	$4\beta \to 8$	33.0	16.1	9.2	8.9	22.5	45.5
(–)-epicatechin	$4\beta \to 8$	36.4	17.8	9.2	8.9	19.0	41.2

Table III
Parameters for the Helices

		$f = 0$			$f = 1$		
monomer	linkage	Rs/Tn[a]	Tran/Rs	pitch	Rs/Tn	Tran/Rs	pitch
(+)-catechin	4α → 8	+4.75	4.84	22.99	−3.16	3.15	9.95
(−)-epicatechin	4α → 8	+5.30	4.85	25.71	−2.89	3.30	9.54
(+)-catechin	4β → 8	+2.95	3.10	9.15	−4.13	4.65	19.20
(−)-epicatechin	4β → 8	+3.00	3.10	9.30	−4.11	4.73	19.44

[a] Rs/Tn is the number of residues per turn, Tran/Rs is the translation per residue in Å, and the pitch is also in Å. A negative sign on Rs/Tn denotes a left-handed helix, and a positive sign denotes a right-handed helix.

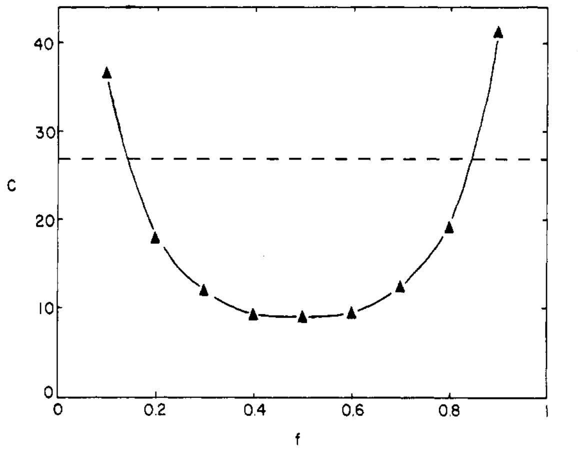

Figure 3. Variation of the asymptotic limit for C with the fraction of the positive rotamer for the homopolymer of (−)-epicatechin with 4β → 8 linkage.

C's are obtained when f is very near 0.5. Characteristic ratios are depicted as a function of f in Figure 3 for the 4β → 8 linked polymer of (−)-epicatechin. Values for f of 0.25 ± 0.15 and 0.75 ± 0.15 correspond to the experimental results based on time-resolved emission measurements for (−)-epicatechin-(4β → 8)-(+)-catechin.[15,16] Since experimental results do not identify the individual rotamers, but only their relative population, the time-resolved emission does not distinguish between $f = 0.25 \pm 0.15$ and 0.75 ± 0.15.

Table II shows that the unperturbed dimensions are affected very little by the substitution of one monomer unit for the other. Larger dimensions are seen in the 4α → 8 linked polymers than in 4β → 8 linked polymers. The origin of the effect of the stereochemistry at C(4) can be traced to the differences in the preferred conformation of the heterocyclic ring. In particular, the attention should be focused on the dihedral angle at bonds 3 and 7 in the structure depicted in Figure 2. The largest dimensions would be expected if this dihedral angle were 180°, signifying a trans arrangement for bonds 2–4 and bonds 6–8. This dihedral angle is 114° in 4β → 8 linked polymers, but it is −125° or −135° in 4 α → 8 linked polymers, depending on the rotational isomer occupied. The puckering of the heterocyclic ring causes the arrangement of bonds 2–4 and 6–8 to be closer to a trans conformation in the 4α → 8 linked polymers, and these polymers therefore have the larger dimensions.

Porter[2] observed that peracetylated proanthocyanidin polymers in tetrahydrofuran behave as though they are more compact than atactic polystyrene chains of the same molecular weight. In order to facilitate comparison on the basis of molecular weight, numerical values in Å^2 have been inserted for the average of l_i^2, and n is replaced by the ratio of the molecular weight of the chain to the average mass per bond in the backbone. The expressions for the mean square unperturbed dimensions of very long polystyrene chains, underivatized proanthocyanidin polymers, and peracetylated proanthocyanidin polymers are then given by eq 6–8, respectively. Using a value of 10 for C for

$$\langle r^2 \rangle_0 = 0.046CM \tag{6}$$

$$\langle r^2 \rangle_0 = 0.030CM \tag{7}$$

$$\langle r^2 \rangle_0 = 0.017CM \tag{8}$$

atactic polystyrene,[21] one concludes that the proanthocyanidin polymers should have $C = 27$ if polystyrene and peracetylated proanthocyanidin polymers of the same M were to have the same unperturbed dimensions. A dashed horizontal line is drawn at $C = 27$ in Figure 3. The 4β → 8 linked polymers are predicted to have C appreciably smaller than 27 when f is 0.25 or 0.75. Therefore Porter's observation[2] is compatible with the expected behavior of the unperturbed chains. Of course, tetrahydrofuran is not a Θ-solvent, and preferential solvent interactions might also affect the dimensions.

As f goes to zero or one, the chain is locked into a single rotational isomer. If the geometry of a rotational isomer is completely rigid, C will then diverge as n becomes infinite. However, the geometry of a rotational isomer is not completely rigid because of the nonzero width of the potential energy wells. Near the minima, the energy, E, for a slight displacement of the dihedral angle at bond 4 in Figure 2 from the energy minimum can be approximated by[12]

$$E - E_{\min} = k(\phi - \phi_{\min})^2 \tag{9}$$

For the homopolymer of (−)-epicatechin with 4β → 8 linkages, the values of k are 13–14 kcal/(mol rad^2).[12] If independent fluctuations in these wells are allowed, the $\sin \phi$ and $\cos \phi$ in the transformation matrices for the interflavan bonds are replaced by $\langle \sin \phi \rangle$ and $\langle \cos \phi \rangle$.[22] At 25–100 °C, this substitution changes C by less than 5% when $0.1 < f < 0.9$, which is the range covered in Figure 3. There is a large effect at $f = 0$ or 1 because the fluctuations within a well cause C to converge as n becomes infinite, where C must diverge in the absence of fluctuations. However, the limiting C's are extremely large (greater than 145). If the only source of flexibility is the fluctuation within the potential well for a single rotational isomer, the chains would be highly extended. Their dimensions would be much larger than those observed with polystyrene of the same molecular weight.

Helices. Table III presents the parameters for the helices obtained when one rotamer is populated to the exclusion of the other. The handedness of the helix is complete determined by the identity of the rotamer selected for propagation of the helix. All polymers considered form right-handed helices when $f = 0$. The stereochemistry at C(3), i.e., selection of (+)-catechin or (−)-epicatechin, and the stereochemistry at C(4), i.e., selection of an α or β linkage, have no effect on the handedness of the helix. The pitch and extension of the helix are sensitive to both the value of f and the stereochemistry at C(4). The

Table IV
Components (in Å) of the Persistence Vector[a]

linkage	monomer	f	$\langle X \rangle$	$\langle Y \rangle$	$\langle Z \rangle$
α	(+)-catechin	0	271.66	178.27	96.10
		0.2	26.54	16.24	14.40
		0.5	9.30	10.14	11.17
		0.8	10.04	30.67	21.53
		1	40.71	194.01	96.37
α	(−)-epicatechin	0	291.63	154.59	84.96
		0.2	23.92	12.08	12.78
		0.5	9.47	10.29	11.48
		0.8	12.75	35.47	24.24
		1	56.76	199.00	104.98
β	(+)-catechin	0	46.36	179.37	−122.69
		0.2	7.06	16.61	−14.55
		0.5	7.21	5.06	−7.92
		0.8	19.43	6.38	−10.20
		1	299.09	102.03	−96.85
β	(−)-epicatechin	0	46.90	179.40	−111.21
		0.2	7.83	17.56	−15.19
		0.5	6.86	4.66	−7.64
		0.8	17.57	4.16	−8.69
		1	298.61	105.04	−97.32

[a] As n approaches infinity for $0 < f < 1$, at $n = 70$ for $f = 0$ or 1.

largest pitches, and the largest translations per monomer unit, are obtained with α link, $f = 0$, and with β link, $f = 1$. In no case does the simple substitution of (−)-epicatechin for (+)-catechin have an important effect on the geometry of the helix.

The direction of the propagation of a helix from the first monomer unit is specified by the entries for $f = 0$ or 1 in Table IV. The components of the vector from the C(8) at one end of bone 1 in Figure 2 to C(4) of the monomer 69 units away are expressed in the local coordinate system defined by bonds 1 and 2. The X axis is in the direction of bond 1, the Y axis is in the plane of bonds 1 and 2, with a positive projection on bond 2, and the Z axis completes a right-handed Cartesian coordinate system.

All helices propagate in the positive X and Y directions, and the sign of the Z component is determined solely by the stereochemistry of the interflavan link at C(4). The molecular basis for these effects is easily seen with the aid of Figure 2. First consider the zeroth-order approximation in which all fused ring systems are precisely planar, the interflavan bond lies in this plane, and all bond angles are 120° for the bonds highlighted in Figure 2. When all highlighted bonds have trans placements, the main chain is then confined to the XY plane of the coordinate system depicted in Figure 2. The signs of X and Y components of the remote chain end are both positive, and these signs are unaffected by reassignment of the dihedral angles at the interflavan bonds.

A better approximation recognizes that the heterocyclic ring is not aromatic and hence the fused ring system is not planar. The sp^3 hybridization at C(4) in the first monomer requires that bond 4 have a significant nonzero Z component, and the sign of this component will depend on the stereochemistry at C(4). Hence, the sign of the Z component in Table IV is determined by the choice of an α or β link, i.e., by the stereochemistry at C(4).

The size of the X component is much more sensitive to f than is either the Y or Z component. The molecular basis for this effect is illustrated in Figure 4. This figure depicts Newman projections for the view from C(4) at one end of bond 4 in Figure 2 to C(8) at the other end. In good approximation, the X axis is parallel to the C(10)–C(5) bond, which is the solid vertical line in each of the four Newman projections. The main chain highlighted in Figure 2 will leave the Newman projection via the bond from C(8) to C(9). This bond is depicted as a dashed line in Figure 4. It is apparent that the projection of C(8)–C(9) on C(10)–C(5), and hence on the X axis, is largest with the combinations α, $f = 0$, and β, $f = 1$.

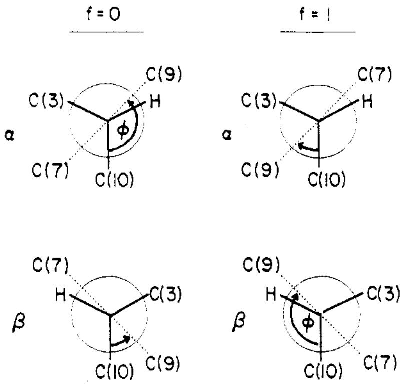

Figure 4. Newman projections for bond 4 in Figure 2 with α or β links and the positive and negative rotamers.

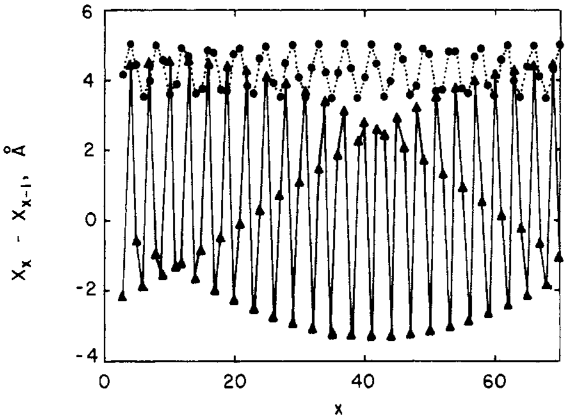

Figure 5. Behavior of $X_x - X_{x-1}$ for rigid helices formed by propagation of a single rotational isomer in homopolymers of (+)-catechin with $4\beta \rightarrow 8$ linkages. The f values are 0 (triangles) and 1 (circles).

Persistence Vectors. The components of persistence vectors at three intermediate f's are also tabulated in Table IV. Two values of f (0.2 and 0.8) are in the range defined by the time-resolved fluorescence measurements,[15,16] and the third value (0.5) describes a chain in which there is equal probability for occupation of either rotational isomer. The signs of the components of the persistence vectors are independent of f; they depend only on the stereochemistry at C(4). The absolute values of these components pass through a minimum as f increases from 0 to 1.

Figure 5 depicts $X_x - X_{x-1}$ for the helices formed by the $4\beta \rightarrow 8$ linked polymer of (+)-catechin when $f = 0$ or 1. All values are positive when f is 1, which accounts for the large X component for the helix in Table IV. Both positive and negative values are obtained when f is 0, and hence Table IV shows a much smaller X component for this helix. The patterns depicted in Figure 5 will propagate indefinitely because each helix is rigid.

Figure 6 depicts $\langle X \rangle_x - \langle X \rangle_{x-1}$ for the same polymer when f is 0.2 or 0.8, the values required by experiment. The oscillatory pattern seen in Figure 5 is rapidly damped when there is a choice of rotational isomers at the interflavan bond. The chain quickly loses all memory of the initial direction established by bond 1.

When allowance is made for rotational isomerism at the interflavan bond, 4–8 linked homopolymers of (+)-catechin and (−)-epicatechin with pseudoequatorial substituents at C(2) are found to be random coils with a small amount of residual helical character. A different conclusion was obtained by Pizzi et al.[19] They assign to all heterocyclic rings

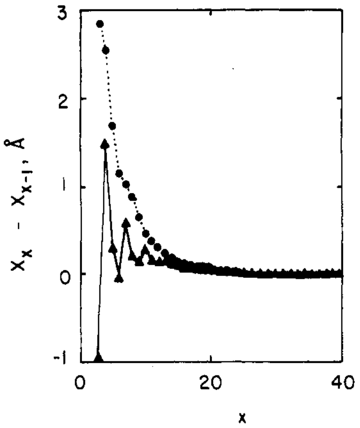

Figure 6. Behavior of $\langle X\rangle_x - \langle X\rangle_{x-1}$ for homopolymers of (+)-catechin with $4\beta \rightarrow 8$ linkages and $f = 0.2$ (triangles) or 0.8 (circles).

the conformation seen in 8-bromotetra-*O*-methyl-(+)-catechin in the crystalline state.[1] This procedure is not supported by crystal structures of other compounds, notably a compound with a phloroglucinol substituent at C(4),[11] nor by MM2 calculations, which indicate there are differences in the ring conformations arising from (i) the nature of linkage (α or β), (ii) rotamer (sign of the linkage torsion), and (iii) relative positions of the monomers in a dimer.[12,13] Pizzi et al. also identify only a single minimum for each dimer. Propagation of the same minimum for each interflavan linkage in a polymer must, of course, generate a helix. The present analysis permits occupation of two rotational isomers in arbitrary ratios and includes assignment of this ratio in the manner demanded by experiment. It also takes into account the ability of the heterocyclic ring to modify its conformation in response to linkage type and assignment of rotational isomer of the interflavan bond.

The formalism described in this work is directly applicable to homopolymers with axial substituents at C(2), and with some modification, it can be applied to C(4)–C(8) linked random or sequential copolymers with α or β linkage types and mixed axial/equatorial C(2) substituents.

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