

Preference for Occupancy of Axial Positions by Substituents bonded to the Heterocyclic Ring in Penta-*O*-acetyl-(+)-catechin in the Crystalline State

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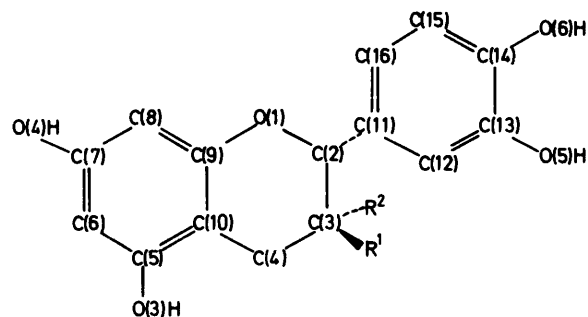
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The structure of penta-*O*-acetyl-(+)-catechin has been determined in the crystalline state. Crystals are monoclinic, space group $C2$, $a = 2\,320.0(7)$, $b = 980.1(2)$, $c = 1\,108.0(3)$ pm, $\beta = 100.64(2)^\circ$, $Z = 4$, $D_c = 1.342$ g cm⁻³, $R = 0.058$ for 1 121 observations. One of the acetyl groups is disordered. Axial positions are occupied by the substituents bonded to heterocyclic ring atoms C(2) and C(3). The substituent bonded to C(2) occupies an equatorial position in previously reported crystal structures for related compounds. The root-mean-square dipole moment is 3.67 ± 0.26 D in dioxane at 25 °C. Conformational analysis demonstrates that the measured dipole moment in dioxane can be expected if either the same ring geometry or a diequatorial form occurs in solution. ¹H N.m.r. coupling constants $J_{2,3}$ 6.5, $J_{3,4}$ 5.0, and $J_{3,4}$ 7.0 Hz suggest a heterocyclic ring conformation between these two extremes or a rapid flexing of the heterocyclic ring in solution at ambient temperature. Spectra recorded at -90 °C do not show a preferred conformation. Instead they show a slow exchange between different conformations of the heterocyclic ring.

Procyanidins are polymers of (+)-catechin¹ and (-)-epicatechin² linked through C(4)-C(6) and/or C(4)-C(8) bonds with number-average molecule weights in the range 3 000–4 000, corresponding to *ca.* 10–14 flavin units (Figure 1). These compounds, together with analogues of different hydroxylation patterns, are wide spread in the plant kingdom.^{1–6} Although earlier views held that these polymers were linear molecules with the catechol B-ring helically coiled about the central core,² evidence now suggests that heterogeneity of the location of interflavanoid bonding results in a less regular structure.^{4,5} Very recent evidence suggests that some of these polymers are branched.^{7–9} Polymeric procyanidins represent the most common class of condensed tannins and, as their name implies, the interaction of these compounds with proteins accounts for much of their biological and economic significance.^{10,11} Recently we initiated a series of studies that have the objective of characterizing the types of interactions that occur between procyanidins and synthetic polypeptides.¹² A successful outcome for this project requires a knowledge of the conformational properties of procyanidin polymers, which in turn demands an understanding of the conformational preferences of the flavan-3-ol monomers.

A crystal structure has been reported for (-)-epicatechin and ¹H n.m.r. spectra, conformational analyses, and dipole moments suggest a similar half-chair conformation in solution.¹³ Parallel analyses of (+)-catechin have not yet been completed. However, the crystal structure of 8-bromotetra-*O*-methyl-(+)-catechin has been reported.¹⁴ Puckering of the heterocyclic ring in (-)-epicatechin and in 8-bromotetra-*O*-methyl-(+)-catechin places the catechol B-ring bonded to C(2) in an equatorial position. The hydroxy function bonded to C(3) is also in an equatorial position in 8-bromotetra-*O*-methyl-(+)-catechin, but it adopts an axial position in (-)-epicatechin. ¹H N.m.r. spectra of the deca-acetates of catechin-(4 α - \rightarrow 8)-catechin and epicatechin-(4 α - \rightarrow 8)-catechin also suggest half-chair conformations of the flavan units with both the catechol B rings and 3-acetoxy groups in quasi-equatorial positions in the catechin



(+)-catechin $R^1 = \text{OH}$, $R^2 = \text{H}$

(-)-epicatechin $R^1 = \text{H}$, $R^2 = \text{OH}$

Figure 1. Structure and numbering system for (+)-catechin and (-)-epicatechin. The oxygen atom denoted O(2) occurs in R^1 for (+)-catechin and in R^2 for (-)-epicatechin

units.¹⁵ Based on these results, one is tempted to hypothesize that the dominant influence on the conformation of the heterocyclic ring in flavan-3-ols and procyanidins is the requirement that the aromatic ring bonded to C(2) be placed in an equatorial position. However, the results reported here show an interesting deviation from this hypothesis since the conformation of penta-*O*-acetyl-(+)-catechin in the crystalline state is such that the substituents bonded to C(2) and C(3) both occupy axial positions.

Results and Discussion

Structure in the Crystalline State.—The crystal structure of penta-*O*-acetyl-(+)-catechin is depicted in Figure 2. Substituents bonded to C(2) and C(3) occupy axial positions. Two half-populated positions are shown for a disordered acetate

bonded to O(3). Co-ordinates for the non-hydrogen atoms are presented in Table 1. Bond lengths and angles are given in Tables 2 and 3.

The heterocyclic ring is depicted in Figure 3 in a manner that facilitates comparison with (-)-epicatechin¹³ and 8-bromotetra-*O*-methyl-(+)-catechin.¹⁴ Puckering of the heterocyclic ring is most apparent at C(2) and C(3). These two atoms lie on opposite sides of the mean plane of the aromatic ring. C(2) is above the mean plane in 8-bromotetra-*O*-methyl-(+)-catechin, but it is below this plane in penta-*O*-acetyl-(+)-catechin. Clearly the conformation of the heterocyclic ring in (+)-catechin derivatives can be influenced by the nature of the substituents present. Examination of the signs of the displacements from the mean plane of the aromatic ring, or of the signs of the dihedral angles, shows that the heterocyclic ring in 8-bromotetra-*O*-methyl-(+)-catechin has more in common with the heterocyclic ring in (-)-epicatechin than that of penta-*O*-acetyl-(+)-catechin. Reversal of the signs of the dihedral angles in the heterocyclic ring in penta-*O*-acetyl-(+)-catechin produces a reasonable approximation to the heterocyclic ring conformation found in (-)-epicatechin. There is a more tenuous relationship to the heterocyclic ring in 8-bromotetra-*O*-methyl-(+)-catechin.

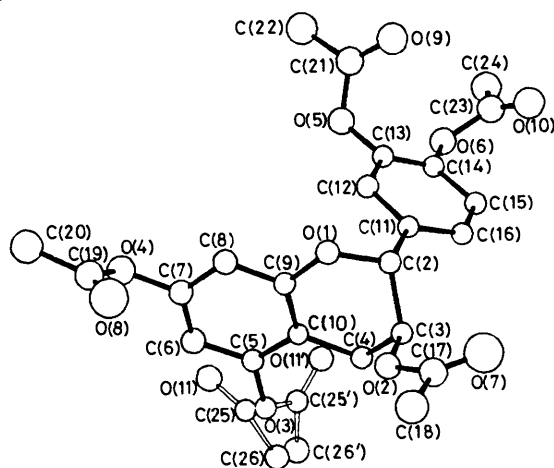


Figure 2. Conformation of penta-*O*-acetyl-(+)-catechin in the crystal

Dipole Moments.—Root-mean-square dipole moments in *p*-dioxane are presented in Table 4. The root-mean-square dipole moment is 3.67 ± 0.26 D at 25 °C. The temperature coefficient is small and probably negative.

Conformational Analysis.—If the rings remain in the conformation seen in the crystalline state, the mean-square dipole moment depends on rotations about six bonds: C(5)–O(3), C(7)–O(4), C(13)–O(5), C(14)–O(6), C(3)–O(2), and C(2)–C(11). The first two rotations are nearly independent of the others. However, the third and fourth are interdependent, as are the fifth and sixth.

Letting θ_A be zero for a *cis*-orientation of C(8)–C(7)–O(4)–C(18), semi-empirical conformational energy calculations find two minima of nearly equal energy when θ_A is +85 and –85°. The first is assigned a weight of w_A relative to the second.

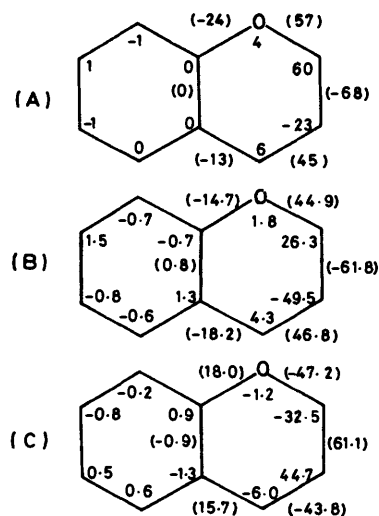


Figure 3. Distances (pm) out of the mean plane of the aromatic ring for atoms in the fused-ring system of crystalline (A) 8-bromotetra-*O*-methyl-(+)-catechin, (B) (-)-epicatechin, and (C) penta-*O*-acetyl-(+)-catechin. Torsion angles (°) for bonds in the heterocyclic ring are denoted by numbers in parentheses. Structural information for (A) and (B) is from refs. 14 and 13, respectively

Table 1. Co-ordinates and isotropic (or equivalent isotropic) thermal parameters for non-hydrogen atoms, penta-acetylcatechin

Atom	x	y	z	B or B_{eq}	Atom	x	y	z	B or B_{eq}
O(1)	0.574 7(2)	0.5270	0.658 0(5)	4.8(1)	C(12)	0.459 8(3)	0.487 3(9)	0.689 2(7)	4.5(2)
O(2)	0.667 8(2)	0.426 8(6)	0.835 3(6)	5.7(2)	C(13)	0.402 0(3)	0.476 9(9)	0.706 8(7)	4.3(2)
O(3)	0.604 3(2)	0.826 1(6)	1.007 2(4)	4.5(1)	C(14)	0.387 4(3)	0.387 8(9)	0.786 4(7)	4.2(2)
O(4)	0.568 2(3)	1.009 8(8)	0.601 8(6)	7.4(2)	C(15)	0.428 8(3)	0.295 7(9)	0.846 7(7)	4.3(2)
O(5)	0.361 9(2)	0.570 5(6)	0.645 7(6)	6.6(2)	C(16)	0.486 3(3)	0.305 5(10)	0.829 1(7)	4.1(2)
O(6)	0.330 8(2)	0.391 2(7)	0.809 1(6)	6.8(2)	C(17)	0.694 8(4)	0.308 7(11)	0.826 1(10)	6.7(3)
O(7)	0.672 2(3)	0.204 7(9)	0.840 2(11)	12.9(3)	C(18)	0.753 7(4)	0.327 3(14)	0.799 6(11)	8.7(3)
O(8)	0.650 3(4)	0.959 1(10)	0.534 8(8)	12.9(3)	C(19)	0.608 4(4)	1.030 4(12)	0.531 8(9)	7.2(3)
O(9)	0.317 0(3)	0.405 7(8)	0.525 5(7)	9.0(2)	C(20)	0.590 3(6)	1.153 9(13)	0.451 4(10)	9.1(4)
O(10)	0.314 5(3)	0.169 7(8)	0.779 8(8)	9.0(2)	C(21)	0.320 7(4)	0.523 3(12)	0.551 4(10)	7.3(3)
C(2)	0.565 6(3)	0.414 8(9)	0.734 1(7)	4.3(2)	C(22)	0.281 3(5)	0.633 0(13)	0.491 7(13)	9.5(4)
C(3)	0.608 5(3)	0.423 4(9)	0.859 3(7)	4.0(2)	C(23)	0.296 1(4)	0.277 4(13)	0.801 2(9)	7.2(3)
C(4)	0.597 8(3)	0.551 9(9)	0.924 5(7)	4.3(2)	C(24)	0.238 2(4)	0.313 7(17)	0.823 5(11)	9.1(4)
C(5)	0.592 8(3)	0.804 1(10)	0.882 4(7)	4.4(2)	O(11)*	0.539 2(5)	1.001 8(15)	1.006 7(11)	6.5(3)
C(6)	0.587 5(4)	0.918 1(10)	0.804 4(8)	5.4(2)	C(25)*	0.572 9(7)	0.917 3(19)	1.061 6(15)	4.5(4)
C(7)	0.577 7(4)	0.892 5(9)	0.679 7(8)	5.1(2)	C(26)*	0.586 3(8)	0.893 0(20)	1.198 7(16)	5.7(4)
C(8)	0.573 3(4)	0.762 2(10)	0.630 4(8)	5.1(2)	O(11')*	0.522 8(5)	0.732 9(13)	1.040 6(11)	5.9(3)
C(9)	0.578 5(3)	0.653 1(9)	0.712 4(7)	4.1(2)	C(25)*	0.565 9(7)	0.794 3(19)	1.076 4(15)	4.7(4)
C(10)	0.589 8(3)	0.672 4(9)	0.838 2(7)	3.7(2)	C(26)*	0.578 1(8)	0.847 4(22)	1.202 7(18)	6.4(5)
C(11)	0.503 0(3)	0.399 5(9)	0.752 4(7)	4.0(2)					

Estimated standard deviations in the least significant digits are shown in parentheses.

* Half populated.

Table 2. Bond lengths (pm) in penta-*O*-acetyl-(+)-catechin

Atoms	Distance	Atoms	Distance
O(1)-C(2)	142.5(8)	C(15)-C(16)	138.7(8)
O(1)-C(9)	137.1(8)	C(16)-C(11)	135.7(9)
C(2)-C(3)	155.3(9)	O(2)-C(17)	132.9(11)
C(2)-C(11)	151.1(9)	C(17)-O(7)	117.1(11)
C(3)-O(2)	145.0(8)	C(17)-C(18)	146.0(11)
C(3)-C(4)	149.6(10)	O(4)-C(19)	133.3(10)
C(4)-C(10)	150.9(9)	C(19)-O(8)	119.3(11)
C(5)-O(3)	137.6(8)	C(19)-C(20)	151.6(14)
C(5)-C(6)	140.3(10)	O(5)-C(21)	136.1(11)
C(5)-C(10)	137.8(10)	C(21)-O(9)	118.7(11)
C(6)-C(7)	138.2(10)	C(21)-C(22)	148.5(13)
C(7)-O(4)	143.0(9)	O(6)-C(23)	137.0(12)
C(7)-C(8)	138.5(10)	C(23)-O(10)	117.9(12)
C(8)-C(9)	139.4(10)	C(23)-C(24)	145.4(13)
C(9)-C(10)	138.3(9)	O(3)-C(25)	136(2)
C(11)-C(12)	140.5(10)	C(25)-O(11)	122(2)
C(12)-C(13)	139.5(9)	C(25)-C(26)	151(3)
C(13)-O(5)	139.0(8)	O(3)-C(25')	132(2)
C(13)-C(14)	132.8(9)	C(25')-O(11')	117(2)
C(14)-O(6)	138.2(8)	C(25')-C(26')	147(3)
C(14)-C(15)	139.5(9)		

Table 3. Bond angles (°) in penta-*O*-acetyl-(+)-catechin

Atoms	Angle	Atoms	Angle
C(2)-O(1)-C(9)	116.1(5)	C(2)-C(11)-C(16)	122.9(6)
C(3)-O(2)-C(17)	118.1(6)	C(12)-C(11)-C(16)	118.0(6)
C(5)-O(3)-C(25)	121.8(8)	C(11)-C(12)-C(13)	120.1(7)
C(5)-O(3)-C(25')	121.5(8)	O(5)-C(13)-C(12)	117.2(7)
C(7)-O(4)-C(19)	115.3(7)	O(5)-C(13)-C(14)	121.9(6)
C(13)-O(5)-C(21)	117.5(7)	O(12)-C(13)-C(14)	120.7(7)
C(14)-O(6)-C(23)	122.4(7)	O(6)-C(14)-C(13)	118.1(7)
O(1)-C(2)-C(3)	110.3(6)	O(6)-C(14)-C(15)	121.4(7)
O(1)-C(2)-C(11)	114.1(6)	C(13)-C(14)-C(15)	120.5(6)
C(3)-C(2)-C(11)	111.0(5)	C(14)-C(15)-C(16)	118.8(6)
O(2)-C(3)-C(2)	108.1(5)	C(11)-C(16)-C(15)	121.9(7)
O(2)-C(3)-C(4)	108.5(6)	O(2)-C(17)-O(7)	121.2(8)
C(2)-C(3)-C(4)	109.9(6)	O(2)-C(17)-C(18)	112.2(9)
C(3)-C(4)-C(10)	111.4(6)	O(7)-C(17)-C(18)	127(1)
O(3)-C(5)-C(6)	118.2(7)	O(4)-C(19)-O(8)	123(1)
O(3)-C(5)-C(10)	119.4(7)	O(4)-C(19)-C(20)	108(1)
C(6)-C(5)-C(10)	122.3(7)	O(8)-C(19)-C(20)	128(1)
C(5)-C(6)-C(7)	116.8(8)	O(5)-C(21)-O(9)	121.7(8)
O(4)-C(7)-C(6)	115.9(7)	O(5)-C(21)-C(22)	113(1)
O(4)-C(7)-C(8)	120.8(7)	O(9)-C(21)-C(22)	126(1)
C(6)-C(7)-C(8)	123.2(7)	O(6)-C(23)-O(10)	120.8(9)
C(7)-C(8)-C(9)	117.3(7)	O(6)-C(23)-C(24)	110(1)
O(1)-C(9)-C(8)	114.5(6)	O(10)-C(23)-C(24)	129(1)
O(1)-C(9)-C(10)	123.5(6)	O(3)-C(25)-O(11)	125(1)
C(8)-C(9)-C(10)	122.0(7)	O(3)-C(25)-C(26)	108(1)
C(4)-C(10)-C(5)	121.1(6)	O(11)-C(25)-C(26)	127(2)
C(4)-C(10)-C(9)	120.7(6)	O(3)-C(25')-O(11')	124(2)
C(5)-C(10)-C(9)	118.3(7)	O(3)-C(25')-C(26')	116(2)
C(2)-C(11)-C(12)	119.1(6)	O(11')-C(25')-C(26')	120(2)

The zero for θ_B is assigned when there is a *cis*-orientation for C(6)-C(5)-O(2)-C(25). Two minima of nearly equal energy are found when θ_B is 80 or -80°. The former has a weight of w_B relative to the latter. Four nearly equivalent minima are found for the interdependent rotations about C(13)-O(5) and C(14)-O(6). The two minima that place the ester groups on opposite sides of the ring are each assigned a weight of one, and the two minima having the ester groups on the same side of the ring each have a statistical weight of w_C . Four minima are also found for the interdependent rotations about C(2)-C(11) and C(3)-O(2). Letting θ_D be zero for a *cis*-orientation of C(2)-C(3)-

Table 4. Dipole moments of penta-*O*-acetyl-(+)-catechin in *p*-dioxane

$t/^\circ\text{C}$	$\langle\mu^2\rangle_0^{1/2}/\text{D}$
15	3.73 ± 0.24
20	3.70 ± 0.25
25	3.67 ± 0.26
30	3.63 ± 0.26

O(2)-C(17), two minima are found at 80 and 160°. The second carries a statistical weight of w_D relative to the first. Nearly equivalent minima are obtained upon a 180° rotation about C(2)-C(11).

If the calculated conformational energy surfaces are used to assign values for the statistical weights *via* $w_i = \exp(-E_i/RT)$, the weights at 300 K would be $w_A = 0.5$, $w_B = 0.5$, $w_C = 0.7$, and $w_D = 0.5$. Since all of these weights are near one, all 64 conformations are expected to be populated to a significant extent in dilute solution. Dipole moments for individual conformations range from 0.93 to 5.87 D. If all 64 conformations are equally populated, the root-mean-square dipole moment is 3.50 D and the temperature coefficient is zero. The average is close to the experimental result reported in Table 4. If the weighting scheme is changed to $w_A = w_B = w_D = 0.5$, $w_C = 0.7$, the root-mean-square dipole moment increases to 3.60 D. The small increase moves the calculated dipole moment closer to the middle of the range defined by experiment. With the modified statistical weights, the temperature coefficient is predicted to be small and negative.

The behaviour of the dipole moments is that expected if the conformation of the heterocyclic ring is the same in the crystal and in dioxane solution. However, the dipole moment data are not a conclusive indicator of conformation for penta-*O*-acetyl-(+)-epicatechin. An additional set of rotational isomeric state calculations was performed for molecules in which the puckering of the heterocyclic ring was modified so that the aromatic ring bonded to C(2) occupied an equatorial, rather than axial, position. These calculations also predict a root-mean-square dipole moment near 3.5 D. Penta-*O*-acetyl-(+)-epicatechin molecules with either heterocyclic ring structure have access to a large number of low-energy rotational isomers. For this reason, the root-mean-square dipole moment is not very sensitive to plausible variation in the conformation of the heterocyclic ring.

¹H *N.m.r.* Spectra.—If the compound is in a 'reverse half-chair' conformation with diaxial substituents at C(2) and C(3), we would expect coupling constants of about $J_{2,3}$ 2, $J_{3,4a}$ 6.0, and $J_{3,4b}$ 5.0 Hz. However, the spectrum of penta-*O*-acetyl-(+)-catechin, when recorded at 200 MHz at 30 °C, showed δ 5.15 (H-2, d, $J_{2,3}$ 6.5 Hz), 5.25 (H-3, m, $J_{3,4a}$ 5.0, $J_{3,4b}$ 7.0 Hz), and 2.67 and 2.86 (H-4a and -4b, m), therefore precluding a stable 'reverse half-chair' solution conformation. These coupling constants would suggest a C(3)-sofa with the B ring in an approximate equatorial position or an averaging of conformations due to rapid flexing of the heterocyclic ring. Spectra recorded over a wide temperature range suggested the latter explanation. Coupling constants obtained from the compound at +50 °C were very similar to those recorded at 30 °C. However, at -50 and -90 °C both the H-2 and -3 signals collapsed to a broad singlet and the H-4 multiplet also converged to a broad singlet while H-6 and -8 of the phloroglucinol ring remained sharp with nicely defined *meta*-coupling of ca. 2 Hz. These spectra can be interpreted as a slowing of the changes in heterocyclic ring conformation and that preferred conformers are not frozen out at -90 °C.

Experimental

Penta-O-acetyl-(+)-catechin.—The penta-acetate was prepared from (+)-catechin isolated from loblolly pine bark. Crystals from methanol–water had m.p. 130–131 °C (lit.,¹⁶ 131 °C). The specific rotation at 578 nm was 35.5° (c 0.1, CHCl₃) (lit.,³ 39.7°).

X-Ray Structure Determination.—A crystal of dimensions 0.28 × 0.30 × 0.36 mm was used for data collection on an Enraf–Nonius CAD4 diffractometer equipped with Mo-K_α radiation (λ 71.073 pm) and a graphite monochromator. Cell dimensions and crystal orientation were determined by a least-squares fit of the setting angles of 25 reflections having 12° < θ < 13°. Crystal data are: C₂₅H₂₄O₁₁, M = 500.5, monoclinic, space group C2, a = 2 320.0(7), b = 980.1(2), c = 1 103.0(3) pm, β = 100.64(2)°, V = 2 476(2) × 10⁻⁶ pm³, Z = 4, D_c = 1.342 g cm⁻³, μ(Mo-K_α) = 1.00 cm⁻¹, T = 299 K. One quadrant of data having h + k even and 1° < θ < 21.5° was collected by the ω–2θ scan method, employing scan rates varying from 0.26 to 5.0° min⁻¹ in order to measure all significant data with I ≈ 20σ(I). A maximum of 400 s was spent on any single scan. Data reduction included corrections for background, Lorentz, and polarization effects; absorption effects were negligible. Of 1 520 unique data points measured, 1 121 had I > 1σ(I), and were used in the refinement.

The structure was solved using direct methods program RANT,¹⁷ after the failure of MULTAN to effect a solution. The absolute configuration was assumed to be the same at chiral centre C(2) as that experimentally determined for 8-bromotetra-O-methyl-(+)-catechin.¹⁴ One of the acetyl groups was found to be disordered, occupying two equally populated positions related by rotation of ca. 67° about the C(5)–O(3) bond. The weak scattering from the crystal and resulting paucity of data prohibited complete anisotropic refinement and refinement of hydrogen atoms. Refinement was accomplished by full-matrix least-squares based upon F with weights w = c⁻²(F_o), using the Enraf–Nonius SDP.¹⁸ Ring atoms and non-hydrogen atoms of the disordered acetyl group were treated as isotropic, while all other non-hydrogen atoms were treated anisotropically. Hydrogen atoms were located from difference maps and included as fixed contributions. Those of the disordered group were not located. Convergence was achieved, and R = 0.058, R_w = 0.075, and GOF = 1.86 for 1 121 observations and 241 variables. Residual electron density of up to 0.26 eÅ⁻³ was indicative of anisotropy not accounted for in the model.*

Dipole Moments.—Dielectric constants were measured from 15.00 ± 0.04 to 30.00 ± 0.02 °C with a Wiss. Techn. Werkstatt D-812 Weilheim Dipolmeter DM01 operating at 2 MHz with a DFL-2 gold-plated thermostatted cell. The basic instrument design was modified to improve temperature stability and to obtain dielectric constants by directly measuring the cell oscillator circuit frequency with an Eldorado model 1608 frequency counter. Refractive indices were measured over the same temperature range with a Bausch and Lomb precision refractometer. Solutions used for the dielectric measurements ranged from 0.2 to 0.8% by weight. Dipole moments were evaluated by the Guggenheim method.¹⁹ Standard deviations were derived from the least-squares data and used to obtain an estimate of error for the dipole moment through the statistical propagation of error equation. The error

analysis takes into account the fundamental reproducibility of the calibration curve, and the dipole moment error limits are given within the 95% confidence interval.

Conformational Energies.—Conformational energy surfaces were evaluated as the sum of 6–12 potentials, intrinsic torsional potentials, and electrostatic interactions calculated in the monopole approximation using a dielectric constant of 3.5. The dominant contribution to each surface was made by the 6–12 potentials. The dipole moment of the ester group was assigned the magnitude and orientation described by Saiz *et al.*²⁰ Ester groups were maintained in the planar *trans* conformation.

¹H N.m.r. Spectra.—Several samples of penta-O-acetyl-(+)-catechin were examined at 200 MHz and 30 °C in [²H₆]-dioxane, CDCl₃, and (CD₃)₂CO. A series of spectra were recorded at –90, –50, and +50 °C in (CD₃)₂CO.

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* Anisotropic thermal parameters and hydrogen co-ordinates are in Supplementary Publication No. SUP. 56298 (4 pp.). For details, see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.