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Structure of 3,4,5-Trihydroxybenzoic Acid Octyl Ester (Octyl Gallate) Dihydrate at 123 K. A Non-Mesogenic Amphiphilic Molecule

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Abstract

The crystal structure of 3,4,5-trihydroxybenzoic acid octyl ester (octyl gallate) dihydrate, $C_{15}H_{22}O_5 \cdot 2H_2O$, is triclinic, $P\bar{1}$, with $a = 6.617$ (1) [6.648 (1)], $b = 9.956$ (2) [9.995 (3)], $c = 14.088$ (4) [14.327 (7)] Å, $\alpha = 79.08$ (2) [79.78 (3)], $\beta = 85.58$ (3) [86.59 (4)], $\gamma = 70.80$ (2) [70.99 (3)]°, $V = 860.5$ Å³, $Z = 2$, $D_x = 1.229$ [1.183] g cm⁻³, $\lambda(Mo K\alpha) = 0.7093$ Å, $\mu = 0.58$ cm⁻¹, $F(000) = 344$ at 123 K [290 K]. The structure was solved by direct methods and refined to $R(F^2) = 0.059$ for 302 parameters and 3655 observations. The alkyl chain of the molecule is in the fully extended conformation. The molecular packing is head-to-head bilayer with interdigitizing alkyl chains. The gallate head groups are hydrogen bonded with the water molecules to form a strong system of intra- and intermolecular hydrogen bonds consisting of finite and infinite chains. The crystals undergo crystal-to-crystal phase transitions at 365 K on heating and at 333 K on cooling, but despite the molecular packing which is analogous to that of the mesogenic alkyl glycosides, there is no thermotropic liquid crystal phase prior to the formation of the isotropic liquid phases at 376 K. Similarly, no lyotropic liquid crystal phases are observed at room temperature in contact with a mixture of water and propanediol in which the crystals are soluble.

Introduction

The amphiphilic carbohydrates such as the *n*-alkyl 1-*O*- or 1-*S*-pyranosides (Jeffrey, 1984, 1986), *n*-alkyl gluconamides (Pffannemüller, Welte, Chin & Goodby, 1986) and the 1-deoxy-1-(*N*-methylalkamido)-*D*-glucitols (MEGA-*N*) (Goodby, Marcus, Chin, Finn & Pffannemüller, 1988) are mesogens when the alkyl chain length exceeds seven C atoms.

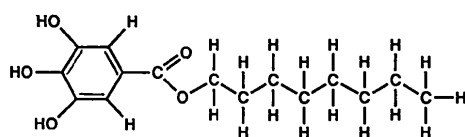
They also undergo one or more crystal-to-crystal phase transitions prior to forming thermotropic liquid crystals of the smectic type in the temperature range 333–463 K. When sufficiently soluble, they form lyotropic liquid crystals at room temperature with water or water–alcohol mixtures. The β -alkyl glucosides, especially *n*-octyl- β -*D*-glucopyranoside, and the glucitol derivatives (MEGA-8 to MEGA-12) are well known surfactants used in the crystallization of membrane proteins (Baron & Thompson, 1975; Hildreth, 1982). *n*-Octyl-1-*O*- β -glucopyranoside has also been shown to have a beneficial effect on the crystal growth of soluble proteins (McPherson, Koszelak, Axelrod, Day, Williams, Robinson, McGrath & Cascio, 1986).

The crystal structures have been determined for anhydrous *n*-octyl-1-*O*- α -*D*-glucopyranoside (van Koningsveld, Jansen & Straathof, 1988) and its hemi- and monohydrate (Jeffrey, Yeon & Abola, 1987), *n*-decyl-1-*O*- α -*D*-glucopyranoside (Moews & Knox, 1976), *n*-heptyl-*S*- α -*D*-mannopyranoside (Carter, Ruble & Jeffrey, 1982), *n*-octyl-1-*O*- β -*D*-xylopyranoside (Bhattacharjee & Jeffrey, 1983), *n*-octyl-*D*-gluconamide (Bhattacharjee, Jeffrey & Goodby, 1985; Zabel, Müller-Fahrnow, Hilgenfeld, Saenger, Pffannemüller, Enkelmann & Welte, 1986), 1-deoxy-(*N*-methylnonamido)-*D*-glucitol (Müller-Fahrnow, Zabel, Steifa & Hilgenfeld, 1986) and 1-deoxy-(*N*-methylundecanamido)- and 1-deoxy-(*N*-methylundecanamido)-*D*-glucitol (Jeffrey & Maluszynska, 1989).

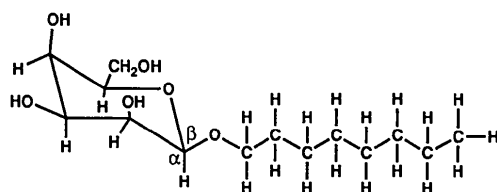
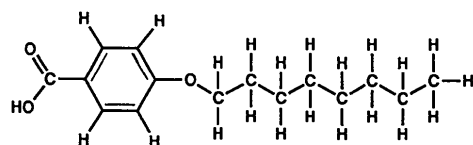
Two types of molecular packing are observed: hydrogen-bonded ‘head-to-head’ bilayers with interdigitizing alkyl chains in the alkyl pyranosides and alkyl gluconamides, and ‘head-to-tail’ monolayers with interdigitizing alkyl chains in the glucitol alkamide derivatives. In both types of structure, the hydrogen bonding is extensive, linking the head

groups into layers which form the hydrophilic core of the bilayer or monolayer structures (*cf.* Gray & Goodby, 1984).

Octyl gallate (I), 3,4,5-trihydroxybenzoic acid octyl ester, is an amphiphilic molecule which is configurationally similar both to *n*-octyl- α - or - β -D-glucopyranoside (II), and *p*-*n*-octyloxybenzoic acid (III) (Bryan, Hartley, Miller & Shen, 1980), all of which form thermotropic liquid crystal phases.



(I) Octyl gallate

(II) *n*-Octyl-1-*O*- α (β)-D-glucopyranoside(III) *p*-*n*-Octyloxybenzoic acid.

On the other hand, some amphiphilic molecules such as 6-*N*-hexylaminopurine and 6-*N*-heptylmercaptopyrine have been shown to have related molecular packing in their crystal structures, but no mesogenic properties (Maluszynska & Jeffrey, 1987). The purpose of this investigation was to establish whether the octyl gallate crystal structure was of the same type as those observed for the alkyl purines or the alkyl carbohydrates or benzoic acids.

Experimental

Recrystallization of a sample of octyl gallate (Fluka Chemical Company) from aqueous ethanol at 277 K gave good diffraction-quality crystals of the dihydrate. The crystallographic, experimental structure determination and structure refinement data are given in Table 1. The intensities were measured on a Nonius CAD-4 diffractometer using Zr-filtered Mo $K\alpha$ radiation by integrating $\omega/2\theta$ scans over 96 intervals. The structure was solved by the direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980).

Table 1. Crystal structure determination and refinement data for octyl gallate dihydrate at 123 K

Crystal data	
Space group	$P\bar{1}$
Z	2
Cell dimensions at 12 K [293 K]	
<i>a</i> (Å)	6.617 (1) [6.648 (1)]
<i>b</i> (Å)	9.956 (2) [9.995 (3)]
<i>c</i> (Å)	14.088 (3) [14.327 (7)]
α (°)	79.08 (2) [79.78 (3)]
β (°)	85.58 (3) [86.59 (4)]
γ (°)	70.80 (2) [70.99 (3)]
μ (cm ⁻¹)	0.58
<i>D_m</i> at 293 K (g cm ⁻³)	1.154
<i>D_x</i> at 123 K [293 K] (g cm ⁻³)	1.229 [1.183]
Experimental data	
Crystal dimensions (mm)	0.54 × 0.35 × 0.23
Number of reflections measured	6420
Number of unique reflections	5001
Number of observed reflections	3656, $F_{\text{obs}} > 3\sigma(F_{\text{obs}})$
Range of <i>h,k,l</i>	-9 ≤ <i>h</i> ≤ 9 -13 ≤ <i>k</i> ≤ 13 0 ≤ <i>l</i> ≤ 19
θ_{max} (°)	60
<i>R</i> (F^2)	0.059
<i>wR</i> (F^2)	0.063
<i>S</i>	1.77
Number of parameters	306
Residual electron difference density (e Å ⁻³)	± 0.15

Structure solution by *MITHRIL* (Gilmore, 1983) using 250 $|E_{h,k,l}| > 1.95$. Function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(F_o)$ from counting statistics. Cell dimensions based on 25 reflections with $9 < \theta < 30^\circ$.

One reflection ($\bar{1}\bar{1}3$) affected by extinction, for which $F_c^2 - F_o^2 > 46.7$, was excluded from the final refinement. All H atoms were located by difference Fourier syntheses and refined with isotropic thermal parameters. One of the water hydroxyl bonds OW1—H2 is disordered over two orientations, giving half-hydrogen occupancy factors for H2 and H2'. The final atomic parameters are given in Table 2. The atomic notation and thermal ellipsoids are shown in Fig. 1.*

The differential calorimetry thermographs, provided by Dr J. Goodby, AT&T Bell Laboratories, are shown in Fig. 2. They show a crystal-to-crystal transition at 365 K on heating, possibly with dehydration, and at 333 K on cooling, but no transition to a liquid crystal phase. This was confirmed by optical microscopy. No lyotropic liquid crystal behavior was observed at room temperature by optical microscopy in contact with a water-propanediol solution in which the crystals slowly dissolved.

* Lists of observed and calculated structure factors and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52661 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic positional and isotropic thermal parameters for octyl gallate dihydrate at 123 K

$B_{eq} = (4/3)\sum_i \beta_i a_i^2$. B_{eq} for non-H atoms in $\text{\AA}^2 \times 10^2$ from the refined anisotropic thermal parameters. B for H atoms in $\text{\AA}^2 \times 10$. E.s.d.'s given in parentheses refer to the least significant digit.

	x	y	z	B_{eq}/B
C1	0.6814 (2)	-0.1362 (2)	0.1711 (1)	149 (8)
C2	0.6098 (3)	0.0081 (2)	0.1833 (1)	152 (8)
C3	0.4122 (2)	-0.0975 (2)	0.1491 (1)	144 (8)
C4	0.2830 (2)	0.0439 (2)	0.1036 (1)	147 (8)
C5	0.3558 (2)	-0.0995 (2)	0.0908 (1)	148 (8)
C6	0.5540 (3)	-0.1899 (2)	0.1241 (1)	154 (9)
C7	0.8868 (3)	-0.2376 (2)	0.2109 (1)	162 (9)
C8	1.1847 (3)	-0.2757 (2)	0.3063 (1)	177 (9)
C9	1.2733 (3)	-0.1890 (2)	0.3583 (1)	169 (9)
C10	1.4779 (3)	-0.2836 (2)	0.4107 (1)	191 (9)
C11	1.5725 (3)	-0.1998 (2)	0.4645 (1)	195 (9)
C12	1.7645 (3)	-0.2952 (2)	0.5248 (1)	225 (10)
C13	1.8589 (3)	-0.2127 (2)	0.5797 (1)	211 (10)
C14	2.0620 (3)	-0.3070 (2)	0.6325 (1)	274 (11)
C15	2.1584 (3)	-0.2229 (2)	0.6857 (1)	328 (13)
O1	0.9862 (2)	-0.1785 (1)	0.2615 (1)	183 (6)
O3	0.3455 (2)	-0.2394 (1)	0.1598 (1)	193 (7)
O4	0.0895 (2)	0.1369 (1)	0.0732 (1)	213 (7)
O5	0.2160 (2)	-0.1429 (1)	0.0469 (1)	202 (7)
O7	0.9587 (2)	-0.3636 (1)	0.2021 (1)	247 (7)
OW1	-0.0315 (2)	0.4369 (1)	0.0939 (1)	216 (7)
OW2	-0.3825 (2)	0.3673 (1)	0.0470 (1)	213 (7)
H(C2)	0.698 (2)	0.041 (2)	0.212 (1)	15 (3)
H(C6)	0.596 (3)	-0.291 (2)	0.117 (1)	22 (4)
H1(C8)	1.281 (3)	-0.315 (2)	0.258 (1)	18 (3)
H2(C8)	1.152 (3)	-0.355 (2)	0.352 (1)	17 (3)
H1(C9)	1.160 (3)	-0.140 (2)	0.404 (1)	15 (3)
H2(C9)	1.305 (3)	-0.111 (2)	0.312 (1)	14 (3)
H1(C10)	1.477 (3)	-0.365 (2)	0.456 (1)	22 (4)
H2(C10)	1.582 (3)	-0.331 (2)	0.365 (1)	21 (3)
H1(C11)	1.453 (3)	-0.147 (2)	0.506 (1)	23 (4)
H2(C11)	1.614 (3)	-0.125 (2)	0.417 (1)	20 (3)
H1(C12)	1.715 (3)	-0.370 (2)	0.571 (1)	25 (4)
H2(C12)	1.882 (3)	-0.354 (2)	0.486 (1)	28 (4)
H1(C13)	1.744 (3)	-0.167 (2)	0.628 (1)	27 (4)
H2(C13)	1.889 (3)	-0.129 (2)	0.532 (1)	19 (3)
H1(C14)	2.024 (3)	-0.384 (2)	0.679 (1)	25 (4)
H2(C14)	2.164 (3)	-0.357 (2)	0.584 (1)	35 (4)
H1(C15)	2.289 (4)	-0.285 (2)	0.711 (2)	47 (5)
H2(C15)	2.053 (3)	-0.183 (2)	0.738 (1)	39 (5)
H3(C15)	2.201 (3)	-0.142 (2)	0.639 (1)	36 (4)
H(O3)	0.227 (3)	0.277 (2)	0.142 (1)	20 (3)
H(O4)	0.033 (3)	0.110 (2)	0.047 (1)	23 (4)
H(O5)	0.283 (3)	-0.215 (2)	0.026 (1)	30 (4)
H1(OW1)	-0.055 (3)	0.495 (2)	0.128 (1)	38 (5)
H2(OW1)*	0.000 (3)	0.460 (2)	0.052 (1)	47 (5)
H3(OW1)*	-0.123 (4)	0.420 (2)	0.086 (1)	34 (5)
H1(OW2)	-0.463 (3)	0.334 (2)	0.089 (1)	33 (4)
H2(OW2)	-0.297 (4)	0.381 (2)	0.068 (2)	58 (6)

*Disordered H atom with 50% occupancy factor.

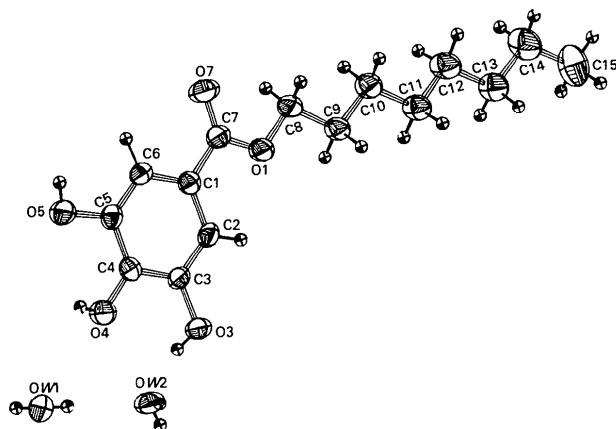


Fig. 1. Atomic notation and thermal ellipsoids (50% probability) for octyl gallate at 123 K.

Discussion

The molecular packing shown in Fig. 3 is typical bilayer head-to-head with interdigitizing alkyl chains, analogous to that of the alkyl 1-*O*- and 1-*S*-glucopyranosides. The head groups are hydrogen bonded with the water molecules to form the bilayer which is approximately perpendicular to the crystallographic *b* axis.

The alkyl chains are fully extended. As shown in Table 3, there is a small twist at C9—C10—C11—C12 of 174.5° , which is compensated at C11—C12—C13—C14 with -174.9° . The other three alkyl-chain torsion angles and the ester torsion angle C7—O1—C8—C9 are within 1.2° of 180° . The C2—C1—C7—O1 torsion angle is 2.8° , so that the plane of the benzene ring is close to that of C7—O7—O1 and the atoms C9 to C15. The respective dihedral angles are $6.1(2)$ and $9.9(1)^\circ$. The best line through the atoms C8...C15 makes

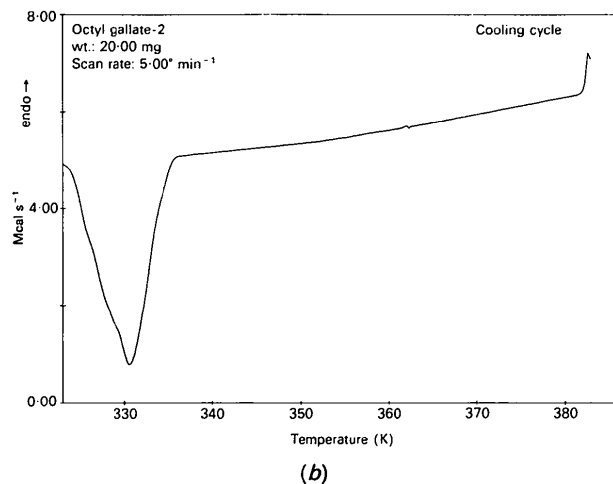
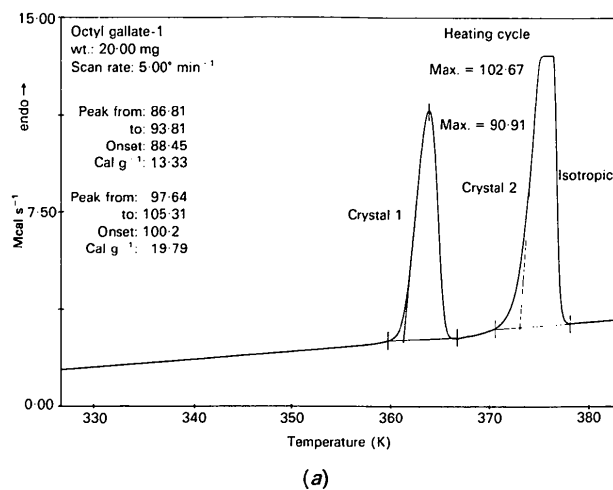


Fig. 2. (a), (b) Differential calorimetry thermograms for octyl gallate, showing no liquid crystal phase transition.

angles of 37.7, 65.6 and 48.0° with the *a*, *b* and *c* axes, respectively.

The molecular dimensions are given in Table 3. The benzyl ring is planar to within 0.007 Å, with a mean deviation from the best plane of 0.004 Å. The C—C bond lengths indicate the quinoidal character, with C2—C3 and C5—C6 0.020 Å shorter than the mean of the other four ring bonds. The carboxylate group is planar to within 0.002 Å. The bond lengths for the carboxylate groups and the alkyl chain are normal. The latter range from 1.505 to 1.527 Å, with a mean value of 1.519 Å. The C—C—C valence angles range from 111.2 to 113.3°. The C7—O1—C8 angle is greater, 115.5°, and the O1—C8—C9 angle is smaller, 107.5°. The observed C—H bond lengths range from 0.91 to 1.04 Å. Those of the O—H bonds are shorter, 0.61 to 0.81 Å. The H—O—H angles are 111 and 113°.

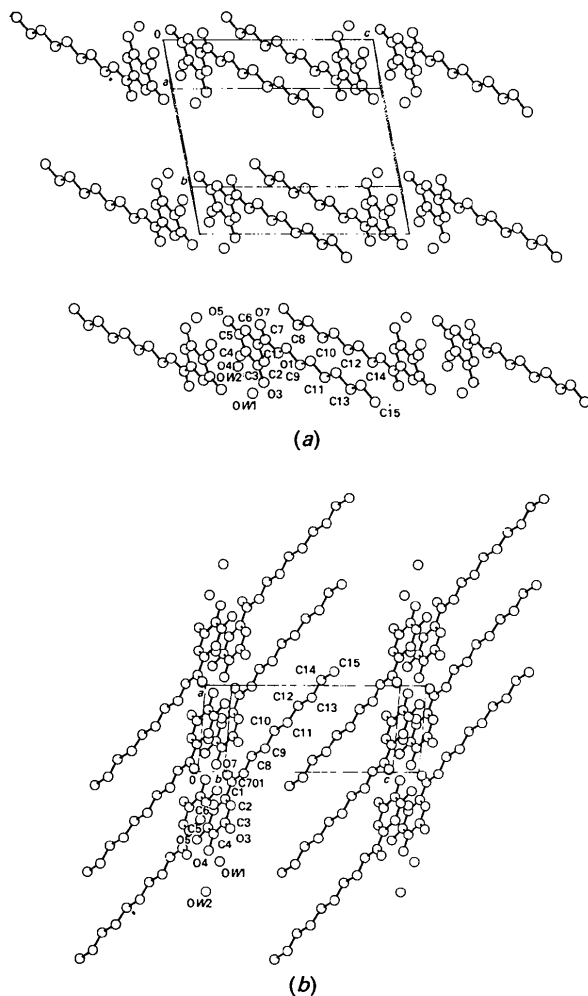
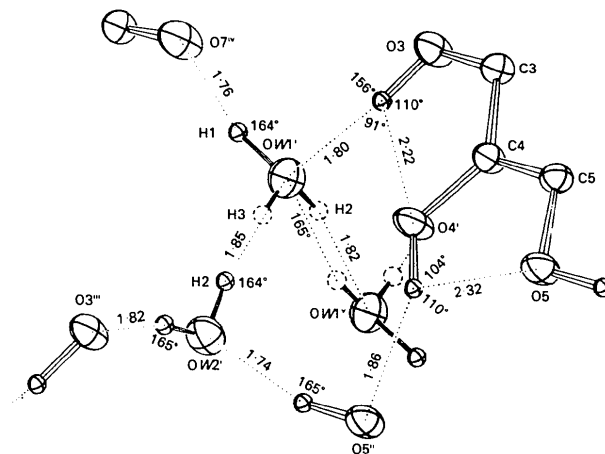


Fig. 3. Molecular packing in the crystal structure of octyl gallate dihydrate: (a) viewed down the *a* axis, with the *c* axis horizontal; (b) viewed down the *b* axis, with the *c* axis horizontal.

Table 3. Selected bond lengths (Å), bond angles (°) and torsion angles (°) in octyl gallate dihydrate at 123 K

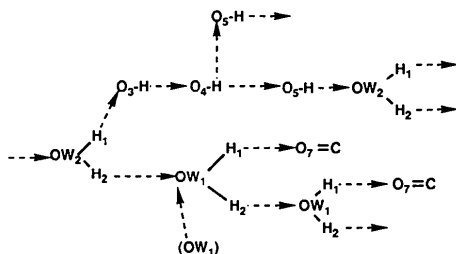
E.s.d.'s given in parentheses refer to the least significant digit.

C1—C2	1.397 (2)	C11—C12	1.518 (3)
C1—C6	1.397 (2)	C12—C13	1.522 (3)
C1—C7	1.477 (2)	C13—C14	1.517 (3)
C2—C3	1.380 (2)	C14—C15	1.527 (3)
C3—C4	1.393 (2)	C3—O3	1.369 (2)
C4—C5	1.391 (2)	C4—O4	1.354 (2)
C5—C6	1.381 (2)	C5—O5	1.370 (2)
C8—C9	1.505 (3)	C7—O1	1.331 (2)
C9—C10	1.522 (3)	C7—O7	1.213 (2)
C10—C11	1.523 (3)	C8—O1	1.456 (2)
C2—C1—C6	120.2 (2)	C1—C6—C5	119.4 (2)
C2—C1—C7	121.6 (2)	C1—C7—O7	124.8 (2)
C6—C1—C7	118.1 (2)	C1—C7—O1	113.2 (2)
C1—C2—C3	119.8 (2)	O1—C7—O7	122.0 (2)
C2—C3—C4	120.2 (2)	C9—C8—O1	107.4 (1)
C2—C3—O3	119.3 (2)	C8—C9—C10	111.1 (2)
C4—C3—O3	120.5 (1)	C9—C10—C11	112.7 (2)
C3—C4—C5	119.8 (2)	C10—C11—C12	113.3 (2)
C3—C4—O4	117.2 (1)	C11—C12—C13	113.7 (2)
C5—C4—O4	123.0 (1)	C12—C13—C14	113.2 (2)
C4—C5—C6	120.5 (2)	C13—C14—C15	112.9 (2)
C4—C5—O5	115.5 (1)	C7—O1—C8	115.5 (1)
C6—C5—O5	123.9 (2)		
C6—C1—C2—C3	0.3 (3)	C3—C4—C5—O5	178.9 (1)
C7—C1—C2—C3	-176.8 (2)	O4—C4—C5—C6	-179.4 (2)
C2—C1—C6—C5	-0.7 (3)	O4—C4—C5—O5	-1.5 (2)
C7—C1—C6—C5	176.5 (2)	C4—C5—C6—C1	0.1 (2)
C2—C1—C7—O7	-177.3 (2)	O5—C5—C6—C1	177.6 (2)
C2—C1—C1—O1	2.8 (2)	C1—C7—O1—C8	177.2 (1)
C6—C1—C7—O7	3.5 (3)	O7—C7—O1—C8	-0.8 (2)
C6—C1—C7—O1	-174.4 (2)	O1—C8—C9—C10	177.9 (1)
C1—C2—C3—C4	0.8 (3)	C9—C8—O1—C7	179.2 (2)
C1—C2—C3—O3	-178.7 (2)	C8—C9—C10—C11	-179.9 (2)
C2—C3—C4—C5	-1.4 (2)	C9—C10—C11—C12	174.5 (2)
C2—C3—C4—O4	178.9 (2)	C10—C11—C12—C13	-179.4 (2)
O3—C3—C4—C5	178.1 (2)	C11—C12—C13—C14	-174.9 (2)
O3—C3—C4—O4	-1.5 (2)	C12—C13—C14—C15	178.8 (2)
C3—C4—C5—C6	1.0 (2)		



The hydrogen bonding

The gallate head groups are hydrogen bonded through the three hydroxyls, the carbonyl group and the two water molecules. All hydrogen-bonding functional groups are involved to form a system of two- and three-center intra- and intermolecular hydrogen bonds. The hydrogen-bonding system, shown in Fig. 4, consists of a series of infinite chains, which branch at the water molecules and at the three-center bond from H(O4). It contains a heterodromic three-bond loop involving both water molecules and H(O3). An unusual feature is the five coordination of the water (W1) which donates two bonds and accepts three; two two-centered and one minor component of a three-center bond. One of the water hydroxyls, OW1—H2, is disordered, forming a quadrilateral arrangement involving half-hydrogen occupancy across the center of symmetry, as shown in Fig. 4. The separation of the half-hydrogen sites is 1.06 Å. This type of hydrogen bonding involving branched infinite chains is similar to that observed in carbohydrate crystal structures (Jeffrey & Mitra, 1983).



Comparison with the crystal structures of *n*-octyl α -D-glucopyranoside and its hydrates

The crystal structure of octyl gallate dihydrate resembles those of *n*-octyl α -D-glucopyranoside and its hemi- and monohydrate (van Koningsveld *et al.*, 1988; Jeffrey *et al.*, 1987) in two respects. One is that the hydrophilic head groups are linked by an extensive system of hydrogen bonds. This forms a layer of hydrogen-bonded structure which is the hydrophilic core of the bilayer arrangement of molecules. The second similarity is that the alkyl chains extend on either side of this bilayer core and interdigitize with those on adjacent bilayers. This structural pattern is found in all the *n*-alkyl pyranosides with $n > 7$ that have been studied hitherto (Jeffrey, 1986), where it is accompanied by thermotropic crystal-to-crystal and crystal-to-mesophase transitions.

Extensive hydrogen bonding is clearly not a deterrent to mesophase properties; neither is it a necessity, as shown by the crystal structures of many other calamitic mesogens (Bryan, 1978) in which hydrogen bonding, where it does occur, is very

limited (as in the *p*-*n*-alkoxybenzoic acid dimers, for example). Neither is a bilayer crystal structure with interdigitizing alkyl chain a necessary precursor to liquid crystal formation, as shown by this example and those of 6-*N*-heptylmercaptapurine and 6-*N*-hexylaminopurine (Maluszynska & Jeffrey, 1987).

The major difference in the molecular packing in the gallate and carbohydrate crystal structures is in the inclination of the alkyl chains to the mid-plane of the bilayer core. In all three crystal forms of the octyl α -glucopyranoside, the angle is close to 90°, whereas in octyl gallate dihydrate, it is 35° (see Fig. 3*b*). A second important difference is in the stacking of the flat benzenoid rings of the gallate molecules *versus* the pyranose chairs.

In the gallate crystal structure there are 18 intermolecular C...C distances between benzene atoms which lie between 3.5 and 4.0 Å across the centers of symmetry. In octyl α -D-glucopyranoside monohydrate, there are no pyranose ring C...C distances less than 4.0 Å. Therefore, in addition to the hydrogen bonding, there are strong van der Waals stacking forces between the head groups in the gallate structure, which do not occur in the pyranoside.

There are two possible explanations for the absence of mesogeneity in octyl gallate dihydrate. One is that the difference in response to thermal energy of the two components of the amphiphile is not appropriate, *i.e.* too large or too small.* The second is that the crystal-to-crystal transition at 365 K involves a change to a crystal structure which is not an appropriate precursor to a mesophase.

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* In this regard, it is interesting to note that in the alkyl pyranosides and the alkamido alditols, the melting points (*i.e.* transition to liquid crystal) are almost independent of alkyl chain length, whereas the clearing points (liquid crystal to isotropic liquid) rise steadily with chain length (Jeffrey, 1986; Goodby *et al.*, 1988). This suggests that the hydrogen-bonded head groups 'melt' before the alkyl chains in the carbohydrate mesogens.

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The Conformation of Nine-Membered Rings

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Abstract

Each of the 16 symmetrical conformations of puckered nine-membered rings is characterized by three amplitude–phase pairs which can be mapped onto the surface of a helical tube that closes into a torus. A projection along the tubular axis, assuming constant radii yields a composite map on which all symmetrical forms can be located unequivocally. The symmetrical forms and representative examples from the literature are analyzed quantitatively in terms of the six primitive forms defined by the three symmetry classes of displacement from a regular planar nonagon.

Introduction

The conformation of an N -membered cyclic compound can be described quantitatively as a linear combination of $N - 3$ primitive forms (Boeyens & Evans, 1989). For small ring systems these are typically the same as the well-known low-energy symmetrical forms, but for large N some of them could present chemically unlikely arrangements (Evans & Boeyens, 1989). As N increases the large number of contributing forms obscures the interpretation of the coefficients in the linear combinations, and for very large rings it is therefore preferable to resort to

different, more intuitive schemes of conformational analysis.

The nine-membered ring is probably the maximum size amenable to analysis by mapping the symmetrical and primitive forms onto an $(N - 3)$ -dimensional surface, projected into two for graphical interpretation, a procedure described before for six-, seven- and eight-membered rings by Boeyens (1978), Boessenkool & Boeyens (1980) and Evans & Boeyens (1988), respectively.

Method

The low-energy forms of nine-membered rings and their modes of interconversion were first analyzed by Hendrickson (1964, 1967).

The set of symmetrical conformations need not be limited to the low-energy cycloalkane conformations. Steric factors and crystal-packing forces can force a ring to adopt a conformation other than that of the isolated entity. Sixteen symmetrical conformations, some based on molecular models, have been identified here, including the six conformations detailed by Hendrickson (1964) or postulated as intermediates. These forms are not representative of a particular chemical system, but their bond lengths and angles are within the limits of chemical viability, and