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Inclusion of the Main Pheromone Component of *Dacus oleae*, 1,7-Dioxaspiro[5,5]undecane, in β-Cyclodextrin

Nicole Rysanek, Geneviève Le Bas, Françoise Villain and Georges Tsoucaris

ERS 128 CNRS, Centre pharmaceutique, Université Paris XI, Avenue JB Clément, 92290 Châtenay Malabry, France

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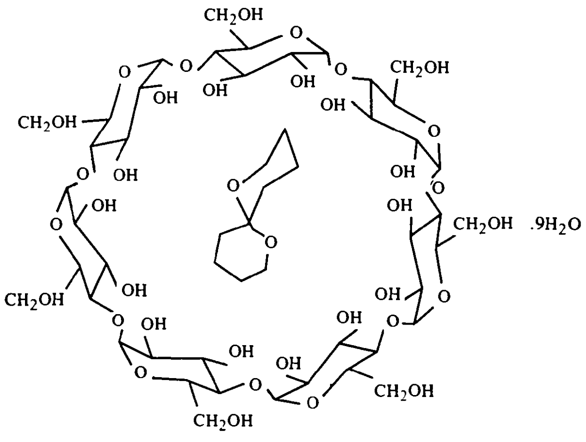
Abstract

The complex β-cyclodextrin–1,7-dioxaspiro[5,5]undecane nonahydrate, $C_{42}H_{70}O_{35}.C_9H_{16}O_2.9H_2O$, belongs to the class of β-cyclodextrin dimeric-type complexes. The racemic guest molecule is present in a disordered position. Both enantiomers are located in two different regions inside the channel formed by the host dimers.

Comment

The cyclodextrin (CD) cyclic oligosaccharides are well known for their ability to form inclusion complexes with a variety of guest molecules (Szejtli, 1989). The present guest is the synthetic racemate of (*R*)- and (*S*)-1,7-dioxaspiro[5,5]undecane (spiroacetal) which constitutes the major component of the olive fruit fly (*Dacus oleae*) pheromone (Baker *et al.*, 1980; Mazomenos & Haniotakis, 1981,1985). It is a liquid too volatile at ambient temperature to be used by itself in agriculture. Previous experiments have shown that there is stabilization upon complexation but the release rate for the β-CD–spiroacetal crystalline complex is almost negligible in dry conditions; the commercial methylated-CD–spiroacetal complexes lead to higher rates, although still too low for practical applications (Mazomenos, Kondilis, Moustakali, Hadjoudis & Tsoucaris, 1989). The crystal-structure determination of the title complex, (I), was undertaken to obtain information on the slow-release process for this pheromone component. Of further interest is the enantiomeric discrimination of the guest molecule by cyclodextrins.



(I)

The title complex crystallizes in the non-centrosymmetric space group *C*2; isomorphous structures have been already studied (Hamilton, Sabesan & Steinrauf, 1981; Hamilton & Sabesan, 1982; Le Bas, 1985). Normal values are observed for the bond lengths and angles of β-CD host molecule. The torsion angles controlling the orientation of the C6—O6 bonds indicate a *gauche–gauche* conformation for all residues. However, two primary hydroxyl groups, O62 and O65, are disordered over two sites; a *trans–gauche* conformation is observed for the minor site O65B while O62 exhibits positional disorder (Table 2).

The macrocyclic ring has the usual truncated-cone shape with a pseudo-sevenfold axis; the glycosidic O4*n* atoms (*n* = 1–7) form a planar heptagon whose sides have an average length of 4.37 (1) Å. The O4*n* atoms deviate by 0.014 Å from their optimum plane. The O4*n* atoms furthest from the centre *I* are almost opposite positions to each other [O43···*I* 5.21 (1), O47···*I* 5.31 (1) Å]; the shortest distances are O45···*I* 4.88 (1) and O42···*I* 4.97 (1) Å. This gives the cavity a slightly elliptical shape and could be related to the shape of the guest molecule. The average intramolecular distances between secondary O atoms are O3*n*···O2(*n*+1) 2.82 Å and average angles are C3*n*—O3*n*···O2(*n*+1) 116° and C2(*n*+1)—O2(*n*+1)···O3*n* 118 Å; these values correspond to intramolecular hydrogen bonds (hydrogen bonds are defined on the basis of O···O distances shorter than 3.0 Å and C—O···O angles greater than 100°). This structure belongs to the class of β-CD dimers already described in detail (Le Bas, 1985; Le Bas & Rysanek, 1987). This class of structures is characterized by the packing of the β-CD dimers in quasi-invariant layers (Le Bas, 1985; Le Bas & Tsoucaris, 1994). Two β-CD molecules related by the twofold crystallographic *b* axis form a head-to-head dimer. Face-to-face secondary hydroxyl groups are bound by seven hydrogen bonds [average distance O3*n*···O3$n^{\rm i}$ 2.80 Å, average angle C3*n*—O3*n*···O3$n^{\rm i}$ 118°; symmetry code: (i) $-x, y, -z+1$]. The axis of the dimers, defined as

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the normal to the average O4*n* plane, is tilted by an angle of 7° relative to the crystallographic *c* axis. The dihedral angle between average O4*n* planes and the *ab* plane is 10.2°. The dimers form layers parallel to the *ab* plane. The stacking of the layers gives rise to continuous channels of dimers along the *c* axis. Successive dimers within a channel are directly linked by a hydrogen bond between the primary hydroxyl groups (Table 3). Adjacent channels are held together by intermolecular hydroxyl bonding (Table 3) as well as through water molecules; all primary hydroxyls are attached to at least one water molecule *via* a hydrogen bond (Table 4). There are nine water molecules distributed over 16 sites in the asymmetric unit (some partially occupied sites are mutually exclusive).

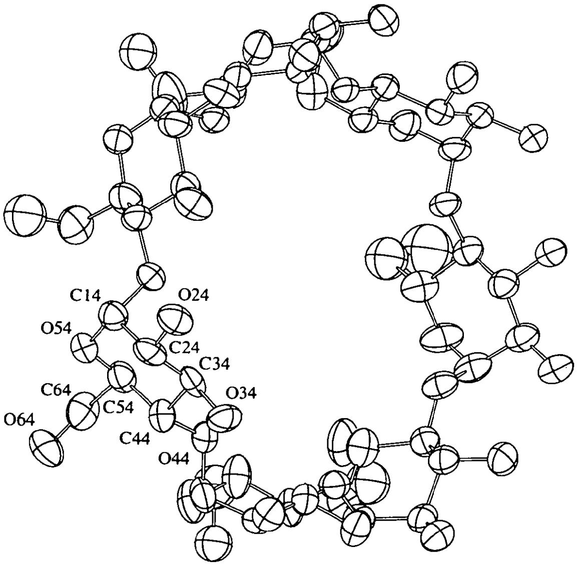

Fig. 1. *ORTEP*II (Johnson, 1976) view of the β-cyclodextrin molecule with atom-numbering scheme for glucose residue number 4. Displacement ellipsoids are plotted at the 50% probability level.

The guest molecules, which are completely enclosed within the β-CD channel, are located in two regions. In the first (region *A*, intradimer or secondary level), the guest is enclosed in the cage between the two moieties of the CD dimer, lying across the channel. Distances from the nearest guest atoms to two successive O4*n*–CD planes are 2.1 and 2.6 Å. In the second region (region *B*, primary level), located between two CD dimers, the guest molecule is aligned along the channel and inserted deep into one CD cavity from the primary hydroxyl O6*n* side. Distances from the nearest guest atoms to two successive O4*n*–CD planes are 0.7 and 3.2 Å. In each region, either the *R* enantiomer or the *S* enantiomer can be present with the same occupancy factor; only van der Waals contacts are observed between the host and guest molecules (Table 5). The twofold axis generates an almost-superimposed symmetry-related site; therefore in each region there are four possible sites which cannot be occupied simultanously. Some of the closest sites in regions *A* and *B* are mutually exclusive, and this allows the determination of which sites may be occupied simultaneously along the channel: (1) enantiomer *R* or *S* in region *A* and enantiomer *R* or *S* in region *B*; (2) enantiomer $R^{\rm i}$ or $S^{\rm i}$ in *A* and enantiomer $R^{\rm ii}$ or $S^{\rm ii}$ in *B* [symmetry codes: (i) $-x, y, -z+1$; (ii) $-x, y, -z$]. Consequently, the inclusion complex is composed of two β-CD molecules and two guest molecules.

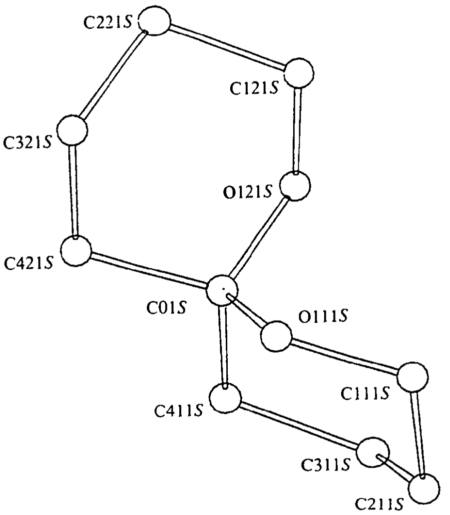

Fig. 2. *ORTEP*II (Johnson, 1976) view of the 1,7-dioxaspiro[5,5]undecane molecule with atom-numbering scheme for enantiomer *S* in region *B*.

The structure described above can account for the great stability of the inclusion complex. The CD channels are embedded in a dense network of hydrogen bonds involving the β-CD hydroxyl groups and water molecules; the guest molecules are held into continuous channels of β-CD molcules. The guest molecule in region *A* locks the channel and probably prevents the second one in region *B* from leaving the channel. It can therefore be expected that the resulting structure is very unfavourable to the spontaneous release of a guest molecule.

In the structure of the unsymmetrical methylated β-CD (or 'overmethylated β-CD') which lacks the sevenfold symmetry and which crystallizes in the triclinic system, a strong chiral discrimination of the same guest is observed (Rysanek, Le Bas, Villain & Tsoucaris, 1992). In the present structure, the pseudo-sevenfold molecular symmetry and the intramolecular hydrogen bonds which maintain the regular shape of the host do not allow the preferential fit of an enantiomeric guest; on the other hand, the presence of the twofold crys-

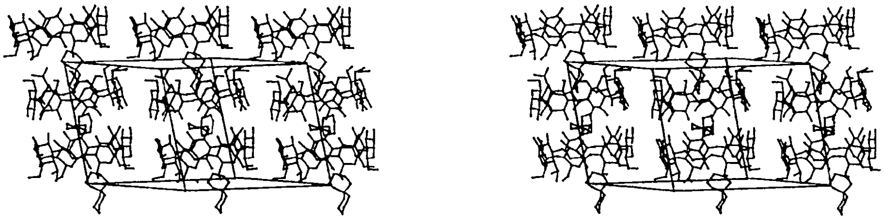

Fig. 3. *SYBYL* (Tripos Associates, Inc., 1988) stereopacking diagram showing the CD channels; for clarity, one guest enantiomer *R* is shown in region *A* and one guest enantiomer *S* is shown in region *B* and water molecules are not shown. (**a** is out of the plane of the paper, **b** horizontal and **c** vertical).

tallographic axis means the two positions of the guest molecule are nearly superimposed. These factors are not favourable for a clear chiral discrimination of the guest.

Experimental

Commercial β-CD and synthesized racemic 1,7-dioxaspiro-[5,5]undecane (spiroacetal) were used to synthesize the title compound. β-CD was dissolved in water to obtain a saturated solution, the solution was mixed with spiroacetal and heated to 283 K. The mixture was cooled slowly to ambient temperature and crystals were obtained. A crystal was sealed in a glass capillary and tested by photographic methods before being mounted on the diffractometer.

Crystal data

$C_{42}H_{70}O_{35}.C_9H_{16}O_2.9H_2O$
$M_r = 1453.37$
Monoclinic
*C*2
$a = 19.368\ (8)$ Å
$b = 24.45\ (1)$ Å
$c = 15.94\ (1)$ Å
$\beta = 108.72\ (4)°$
$V = 7149\ (12)$ Å^3
$Z = 4$
$D_x = 1.351$ Mg m^{-3}
D_m not measured

Cu *Kα* radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 3–40°$
$\mu = 0.924$ mm^{-1}
$T = 293$ K
Parallelepiped
0.6 × 0.5 × 0.3 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/2θ scans
Absorption correction: none
9895 measured reflections
4769 independent reflections
4405 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.031$
$\theta_{\rm max} = 59.8°$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 100 reflections
intensity decay: 8%

Refinement

Refinement on *F*
$R = 0.086$
$wR = 0.086$
$S = 4.04$
4405 reflections
753 parameters
Unit weights applied

$(\Delta/\sigma)_{\rm max} = 0.04$
$\Delta\rho_{\rm max} = 0.40$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.72$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX76* (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	*x*	*y*	*z*	$U_{\rm eq}$
C11	1	0.2171 (6)	0.1984	0.3135 (8)	0.059 (6)
C21	1	0.1977 (5)	0.2279 (4)	0.3877 (7)	0.056 (6)
C31	1	0.1193 (5)	0.2197 (4)	0.3783 (7)	0.051 (5)
C41	1	0.0736 (5)	0.2396 (4)	0.2877 (7)	0.048 (5)
C51	1	0.0968 (5)	0.2123 (4)	0.2158 (7)	0.054 (5)
C61	1	0.0586 (7)	0.2370 (5)	0.1216 (8)	0.072 (7)
O21	1	0.2444 (4)	0.2099 (3)	0.4735 (5)	0.062 (4)
O31	1	0.1008 (4)	0.2494 (3)	0.4462 (5)	0.067 (4)
O41	1	−0.0010 (3)	0.2256 (3)	0.2765 (4)	0.048 (3)
O51	1	0.1735 (4)	0.2179 (3)	0.2305 (5)	0.058 (4)
O61	1	0.0704 (4)	0.2942 (4)	0.1226 (5)	0.078 (5)
C12	1	−0.0546 (6)	0.2669 (4)	0.2481 (8)	0.059 (6)
C22	1	−0.0943 (6)	0.2737 (4)	0.3133 (8)	0.058 (6)
C32	1	−0.1382 (5)	0.2236 (4)	0.3167 (7)	0.051 (5)
C42	1	−0.1883 (6)	0.2118 (4)	0.2229 (7)	0.056 (6)
C52	1	−0.1453 (7)	0.2060 (5)	0.1604 (8)	0.068 (7)
C62	1	−0.1904 (8)	0.1967 (7)	0.0626 (9)	0.106 (10)
O22	1	−0.0426 (4)	0.2854 (3)	0.3995 (5)	0.071 (4)
O32	1	−0.1789 (4)	0.2302 (3)	0.3757 (5)	0.066 (4)
O42	1	0.2275 (4)	0.1621 (3)	0.2269 (5)	0.054 (4)
O52	1	−0.1025 (4)	0.2547 (3)	0.1618 (5)	0.069 (4)
O62*A*	0.67	−0.2339 (8)	0.2341 (7)	0.0220 (11)	0.080
O62*B*	0.33	−0.2497 (16)	0.2554 (14)	0.053 (2)	0.080
C13	1	−0.3030 (6)	0.1625 (5)	0.1907 (7)	0.057 (6)
C23	1	−0.3340 (6)	0.1400 (4)	0.2593 (8)	0.058 (6)
C33	1	−0.3112 (6)	0.0795 (4)	0.2798 (7)	0.057 (6)
C43	1	−0.3348 (6)	0.0486 (4)	0.1959 (7)	0.053 (5)
C53	1	−0.3060 (7)	0.0734 (5)	0.1263 (7)	0.063 (6)
C63	1	−0.3288 (7)	0.0465 (6)	0.0384 (7)	0.081 (8)
O23	1	−0.3122 (4)	0.1732 (3)	0.3375 (5)	0.069 (4)
O33	1	−0.3439 (4)	0.0572 (3)	0.3419 (5)	0.070 (4)
O43	1	−0.3055 (3)	−0.0055 (3)	0.2145 (4)	0.050 (3)
O53	1	−0.3270 (4)	0.1302 (3)	0.1130 (5)	0.063 (4)
O63	1	−0.4039 (6)	0.0454 (4)	−0.0004 (7)	0.11 (3)
C14	1	−0.3533 (6)	−0.0518 (4)	0.1917 (7)	0.061 (5)
C24	1	−0.3359 (6)	−0.0874 (4)	0.2737 (7)	0.055 (6)
C34	1	−0.2596 (6)	−0.1068 (4)	0.2988 (6)	0.051 (5)
C44	1	−0.2479 (5)	−0.1371 (5)	0.2207 (6)	0.050 (5)
C54	1	−0.2720 (6)	−0.1003 (5)	0.1367 (6)	0.056 (6)
C64	1	−0.2741 (6)	−0.1326 (5)	0.0516 (7)	0.067 (7)
O24	1	−0.3508 (4)	−0.0590 (3)	0.3433 (5)	0.063 (4)
O34	1	−0.2442 (4)	−0.1434 (3)	0.3712 (4)	0.061 (4)
O44	1	−0.1726 (3)	−0.1476 (3)	0.2431 (4)	0.055 (4)
O54	1	−0.3444 (4)	−0.0810 (3)	0.1192 (4)	0.053 (4)
O64	1	−0.3257 (5)	−0.1769 (4)	0.0358 (5)	0.080 (5)
C15	1	−0.1500 (6)	−0.2013 (5)	0.2304 (7)	0.065 (7)
C25	1	−0.1005 (6)	−0.2218 (5)	0.3162 (8)	0.063 (6)
C35	1	−0.0288 (5)	−0.1907 (5)	0.3449 (6)	0.051 (5)
C45	1	0.0039 (5)	−0.1919 (5)	0.2707 (7)	0.060 (6)
C55	1	−0.0482 (6)	−0.1671 (6)	0.1892 (7)	0.078 (9)
C65	1	−0.0220 (10)	−0.1715 (7)	0.1062 (12)	0.115 (6)
O25	1	−0.1334 (4)	−0.2222 (3)	0.3829 (5)	0.064 (4)
O35	1	0.0216 (4)	−0.2142 (3)	0.4234 (5)	0.069 (4)
O45	1	0.0699 (4)	−0.1599 (3)	0.2970 (5)	0.058 (4)
O55	1	−0.1152 (4)	−0.2004 (4)	0.1641 (5)	0.077 (5)

O65*A*	0.66	0.0008 (7)	−0.2228 (6)	0.0920 (8)	0.080
O65*B*	0.34	−0.0705 (13)	−0.1597 (11)	0.0322 (16)	0.080
C16	1	0.1348 (6)	−0.1845 (5)	0.2925 (7)	0.058 (6)
C26	1	0.1933 (6)	−0.1773 (4)	0.3824 (7)	0.058 (6)
C36	1	0.2100 (6)	−0.1164 (4)	0.3964 (7)	0.055 (6)
C46	1	0.2306 (6)	−0.0931 (4)	0.3189 (7)	0.053 (6)
C56	1	0.1742 (6)	−0.1051 (6)	0.2304 (7)	0.066 (7)
C66	1	0.1994 (8)	−0.0942 (7)	0.1504 (8)	0.101 (9)
O26	1	0.1716 (4)	−0.2005 (3)	0.4515 (5)	0.067 (4)
O36	1	0.2675 (4)	−0.1081 (3)	0.4768 (5)	0.065 (4)
O46	1	0.2364 (4)	−0.0354 (3)	0.3306 (5)	0.059 (4)
O56	1	0.1561 (4)	−0.1636 (3)	0.2229 (5)	0.068 (5)
O66	1	0.2603 (6)	−0.1256 (5)	0.1547 (7)	0.113 (4)
C17	1	0.3010 (5)	−0.0077 (5)	0.3296 (8)	0.066 (6)
C27	1	0.3287 (6)	0.0253 (5)	0.4119 (7)	0.063 (6)
C37	1	0.2756 (5)	0.0710 (4)	0.4104 (7)	0.055 (5)
C47	1	0.2620 (5)	0.1039 (4)	0.3265 (7)	0.052 (5)
C57	1	0.2381 (7)	0.0668 (5)	0.2452 (7)	0.064 (6)
C67	1	0.2348 (9)	0.0963 (7)	0.1573 (10)	0.110 (5)
O27	1	0.3429 (4)	−0.0060 (3)	0.4896 (5)	0.070 (4)
O37	1	0.3036 (4)	0.1050 (3)	0.4862 (5)	0.066 (4)
O47	1	0.2041 (3)	0.1412 (2)	0.3227 (5)	0.052 (3)
O57	1	0.2901 (4)	0.0231 (3)	0.2542 (5)	0.074 (5)
O67	1	0.3069 (8)	0.1154 (6)	0.1689 (9)	0.182 (5)
O*W*1	1	0	0.4599 (5)	0	0.091 (4)
O*W*2	1	−0.0452 (5)	0.3687 (4)	0.0809 (6)	0.086 (3)
O*W*3	1	0.3983 (6)	−0.0825 (4)	0.1990 (7)	0.115 (3)
O*W*4	1	−0.0900 (6)	0.3710 (5)	0.4774 (7)	0.117 (3)
O*W*5	0.60	0.4227 (7)	0.0286 (6)	0.1799 (9)	0.100
O*W*6	0.50	−0.0833 (10)	0.6767 (8)	0.4564 (12)	0.100
O*W*7	0.50	0.0600 (10)	0.6772 (8)	0.3779 (12)	0.100
O*W*8	0.42	−1/2	0.1381 (14)	0	0.100
O*W*9	0.60	0.0175 (8)	0.4010 (7)	0.3422 (10)	0.100
O*W*10	0.40	0.0109 (13)	0.5494 (11)	0.3584 (17)	0.100
O*W*11	0.50	0.3722 (10)	0.1884 (8)	0.0687 (13)	0.100
O*W*12	0.45	−0.3456 (11)	0.2837 (9)	0.0662 (13)	0.100
O*W*13	0.30	−0.0278 (17)	0.5877 (13)	0.311 (2)	0.100
O*W*14	0.27	0.004 (2)	−0.5246 (13)	0.471 (2)	0.100
O*W*15	0.30	0.0194 (14)	0.5224 (13)	0.416 (2)	0.100
O*W*16	0.19	−0.489 (3)	0.137 (2)	−0.066 (3)	0.100
C01*S*	0.25	−0.0609 (15)	0.0361 (12)	0.053 (2)	0.259 (9)
O111*S*	0.25	−0.0791 (15)	−0.0151 (12)	0.013 (2)	0.259 (9)
C111*S*	0.25	−0.0288 (15)	−0.0339 (12)	−0.026 (2)	0.259 (9)
C211*S*	0.25	−0.0272 (15)	0.0027 (12)	−0.099 (2)	0.259 (9)
C311*S*	0.25	−0.0047 (15)	0.0601 (12)	−0.065 (2)	0.259 (9)
C411*S*	0.25	−0.0566 (15)	0.0805 (12)	−0.015 (2)	0.259 (9)
O121*S*	0.25	0.0080 (15)	0.0369 (12)	0.118 (2)	0.259 (9)
C121*S*	0.25	0.0159 (15)	0.0030 (12)	0.189 (2)	0.259 (9)
C221*S*	0.25	−0.0400 (15)	0.0161 (12)	0.237 (2)	0.259 (9)
C321*S*	0.25	−0.1161 (15)	0.0146 (12)	0.170 (2)	0.259 (9)
C421*S*	0.25	−0.1214 (15)	0.0495 (12)	0.092 (2)	0.259 (9)
C01*R*	0.25	−0.0368 (16)	0.0160 (11)	0.055 (2)	0.238 (9)
O111*R*	0.25	−0.0503 (16)	0.0710 (11)	0.032 (2)	0.238 (9)
C111*R*	0.25	0.0058 (16)	0.0959 (11)	0.009 (2)	0.238 (9)
C211*R*	0.25	0.0137 (16)	0.0702 (11)	−0.071 (2)	0.238 (9)
C311*R*	0.25	0.0321 (16)	0.0100 (11)	−0.056 (2)	0.238 (9)
C411*R*	0.25	−0.0268 (16)	−0.0180 (11)	−0.023 (2)	0.238 (9)
O121*R*	0.25	0.0280 (16)	0.0079 (11)	0.125 (2)	0.238 (9)
C121*R*	0.25	0.0301 (16)	0.0314 (11)	0.204 (2)	0.238 (9)
C221*R*	0.25	−0.0325 (16)	0.0108 (11)	0.236 (2)	0.238 (9)
C321*R*	0.25	−0.1045 (16)	0.0198 (11)	0.163 (2)	0.238 (9)
C421*R*	0.25	−0.1033 (16)	−0.0037 (11)	0.078 (2)	0.238 (9)
C02*S*	0.25	0.0093 (15)	0.0139 (12)	0.5526 (19)	0.261 (9)
O112*S*	0.25	0.0266 (15)	0.0310 (12)	0.4783 (19)	0.261 (9)
C112*S*	0.25	0.0450 (15)	0.0865 (12)	0.4812 (19)	0.261 (9)
C212*S*	0.25	0.1112 (15)	0.0979 (12)	0.5565 (19)	0.261 (9)
C312*S*	0.25	0.0995 (15)	0.0836 (12)	0.6434 (19)	0.261 (9)
C412*S*	0.25	0.0735 (15)	0.0229 (12)	0.6395 (19)	0.261 (9)
O122*S*	0.25	−0.0487 (15)	0.0434 (12)	0.5648 (19)	0.261 (9)
C122*S*	0.25	−0.1141 (15)	0.0386 (12)	0.4978 (19)	0.261 (9)
C222*S*	0.25	−0.1395 (15)	−0.0216 (12)	0.4819 (19)	0.261 (9)
C322*S*	0.25	−0.0791 (15)	−0.0553 (12)	0.4662 (19)	0.261 (9)
C422*S*	0.25	−0.0089 (15)	−0.0469 (12)	0.5374 (19)	0.261 (9)
C02*R*	0.25	0.0189 (17)	0.0246 (11)	0.546 (2)	0.235 (9)
O112*R*	0.25	0.0232 (17)	0.0814 (11)	0.554 (2)	0.235 (9)
C112*R*	0.25	0.0674 (17)	0.1050 (11)	0.510 (2)	0.235 (9)
C212*R*	0.25	0.1435 (17)	0.0861 (11)	0.547 (2)	0.235 (9)
C312*R*	0.25	0.1480 (17)	0.0245 (11)	0.539 (2)	0.233 (9)
C412*R*	0.25	0.0950 (17)	−0.0029 (11)	0.583 (2)	0.235 (9)
O122*R*	0.25	−0.0079 (17)	0.0074 (11)	0.457 (2)	0.235 (9)
C122*R*	0.25	−0.0779 (17)	0.0238 (11)	0.412 (2)	0.235 (9)
C222*R*	0.25	−0.1331 (17)	0.0040 (11)	0.457 (2)	0.235 (9)
C322*R*	0.25	−0.1074 (17)	0.0227 (11)	0.553 (2)	0.235 (9)
C422*R*	0.25	−0.0308 (17)	0.0066 (11)	0.598 (2)	0.235 (9)

Table 2. *Torsion angles involving primary hydroxyl groups (°)*

Residue	C4—C5—C6—O6
1	55.2 (12)
2	63.4 (19), 53.2(16)
3	58.6 (15)
4	61.2 (11)
5	48.7 (18), 168.1(17)
6	59.2 (15)
7	60.4 (15)

Table 3. *Intermolecular hydrogen bonds between dimers (Å)*

O65*A*···O65*A*^{i}	2.92 (2)	O62*A*···O64^{iii}	2.76 (1)
O61···O64^{ii}	2.87 (1)	O21···O26^{iv}	2.77 (1)

Symmetry codes: (i) $-x, y, -z$; (ii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iii) $-\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$.

Table 4. *Water-molecule hydrogen bonds (Å)*

Distances between water molecules and primary OH groups of CD

O61···O*W*2	2.80 (1)	O63···O*W*16	2.77 (5)
O62*A*···O*W*12	2.76 (2)	O64···O*W*2^{iii}	2.82 (1)
O62*A*···O*W*11^{i}	2.83 (2)	O65*A*···O*W*12^{iv}	3.14 (3)
O62*B*···O*W*11^{i}	3.02 (3)	O66···O*W*3	2.75 (2)
O63···O*W*1^{ii}	2.82 (1)	O66···O*W*12^{iv}	3.04 (2)
O63···O*W*8	2.93 (3)	O67···O*W*11	2.95 (2)
O63···O*W*5^{i}	2.79 (2)	O67···O*W*5	3.05 (2)

Distances between water molecules and secondary OH groups of CD

O22···O*W*4	2.74 (2)	O27···O*W*15^{vi}	2.70 (3)
O23···O*W*7^{ii}	2.75 (2)	O27···O*W*14^{vii}	2.89 (4)
O33···O*W*10^{ii}	2.91 (3)	O35···O*W*7^{v}	2.91 (2)
O24···O*W*9^{ii}	2.72 (2)	O36···O*W*4^{iv}	2.80 (1)
O25···O*W*6^{v}	2.77 (2)	O37···O*W*6^{iv}	2.97 (2)

Distances between water molecules

O*W*1···O*W*2	2.85 (1)	O*W*5···O*W*13^{iv}	2.47 (3)
O*W*2···O*W*3^{viii}	2.74 (2)	O*W*6···O*W*7^{ix}	2.55 (3)
O*W*3···O*W*5	2.79 (2)	O*W*7···O*W*13	2.76 (4)
O*W*3···O*W*9^{iv}	2.71 (1)	O*W*9···O*W*14^{xi}	2.82 (4)
O*W*4···O*W*9^{ix}	2.86 (2)	O*W*10···O*W*14^{xi}	2.58 (4)
O*W*4···O*W*14^{x}	3.02 (3)	O*W*11···O*W*12^{i}	3.10 (3)
O*W*5···O*W*10^{iv}	2.85 (3)	O*W*11···O*W*16^{i}	2.60 (6)

Symmetry codes: (i) $-x, y, -z$; (ii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $-\frac{1}{2}-x, y-\frac{1}{2}, -z$; (iv) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (v) $x, y-1, z$; (vi) $\frac{1}{2}-x, y-\frac{1}{2}, 1-z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (viii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (ix) $-x, y, 1-z$; (x) $-x, 1+y, 1-z$; (xi) $x, 1+y, z$.

Table 5. *Host–guest and guest–guest contacts (Å)*

Guest *R* in region *A*

C112*R*···C31	3.82 (3)	C212*R*···O33^{ii}	3.78 (3)
C112*R*···O31	3.78 (3)	C312*R*···C37^{ii}	3.86 (4)
C212*R*···C37	3.88 (4)	C312*R*···C33^{ii}	3.77 (3)
C212*R*···O37	3.57 (4)	C312*R*···O33^{ii}	3.74 (3)
C212*R*···O32^{ii}	3.72 (3)	C322*R*···C37^{ii}	3.68 (4)
C212*R*···C33^{ii}	3.52 (3)		

Guest *S* in region *A*

C222*S*···O34	3.72 (3)	C312*S*···C33^{ii}	3.88 (3)
C222*S*···C34	3.73 (3)	C312*S*···O42^{ii}	3.29 (3)
C322*S*···O34	3.75 (3)	C312*S*···C42^{ii}	3.87 (3)
C322*S*···C34	3.87 (3)	C312*S*···C32^{ii}	3.52 (3)
C212*S*···C32^{ii}	3.62 (3)	C222*S*···C36^{ii}	3.56 (3)
C212*S*···O32^{ii}	3.53 (3)	C222*S*···O36^{ii}	3.48 (3)
C212*S*···O42^{ii}	3.80 (3)		

Guest *R* in region *B*			
C111*R*···C61	3.87 (3)	C411*R*···C66$^{\rm i}$	3.80 (3)
C411*R*···O65*B*	3.74 (4)		
Guest *S* in region *B*			
O111*S*···O65*B*	3.55 (4)	O111*S*···C66$^{\rm i}$	3.48 (3)
C111*S*···O65*B*	3.40 (4)	C111*S*···C65$^{\rm i}$	3.84 (4)
C321*S*···C53	3.80 (3)	C111*S*···O65*B*$^{\rm i}$	3.65 (4)
C421*S*···C63	3.83 (3)	C111*S*···C66$^{\rm i}$	3.58 (3)
C421*S*···C53	3.83 (4)	C411*S*···C67$^{\rm i}$	3.49 (3)
C421*S*···C62	3.82 (3)		
Guest–guest contact			
C221*S*···O112*R*$^{\rm ii}$	3.62 (4)		

Symmetry codes: (i) $-x, y, -z$; (ii) $-x, y, 1 - z$.

In the atom-numbering scheme for the guest molecule, a final digit of 1 indicates primary level region *B* and 2 secondary level *A*; the last character (*R* or *S*) indicates the enantiomer.

The positional parameters (except the primary hydroxyl groups) from an isomorphous complex (β-CD benzophenone; Le Bas, 1985) were used as a starting point. Successive full-matrix least-square refinements and difference Fourier syntheses were performed. The difference Fourier maps showed clearly two regions of electron density but the guest molecule could not be located precisely at this stage. The refined coordinates of the *S* enantiomer from the study of overmethylated CD with the same guest (Rysanek, Le Bas & Tsoucaris, 1992) were used. These coordinates were graphically plotted onto the difference Fourier map using *FRODO* (Jones, Bush, Pflugrath & Saper, 1978) and then refined. The next difference Fourier maps still showed some electron density in this region which could be interpreted as the *R* enantiomer. This enantiomer was built up from the *S*-enantiomer coordinates and plotted onto the difference Fourier map. The refinements were performed using *SHELX*76 (Sheldrick, 1976). For β-CD, all non-H atoms were refined anisotropically except the disordered O6 atoms. H atoms were introduced at calculated non-refined positions; H-atom positions were not introduced for the guest molecule, water molecules or hydroxyl groups of the host molecules. The coordinates of the *R*- and *S*-enantiomers of the guest molecule were refined isotropically in a block rigid group with an occupancy factor of 0.25 for each guest enantiomer in the two regions. The O atoms of water molecules were refined with common isotropic displacement parameters. The numerous atoms in disordered positions explain the relative high value of the *R* index; this is usual for cyclodextrin structures.

Data collection: *SDP-Plus* (B. A. Frenz & Associates, Inc., 1983). Cell refinement: *SDP-Plus*. Data reduction: *SDP-Plus*. Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *FRODO* (Jones *et al.*, 1978), *SYBYL* (Tripos Associates Inc., 1988), *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1216). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-4,5-Dihydroxy-2,3,4,5-tetraphenylcyclopent-2-enone

Marek J. Jedrzejas,† Marc D. Rubin, Ronald J. Baker, John Masnovi and Robert L. R. Towns

Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA. E-mail: r.j.baker@popmail.csuohio.edu

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Abstract

The title compound, $C_{29}H_{22}O_3$, was prepared by the oxidation of tetraphenylcyclopentadienone with tetranitromethane. The cyclopentenone ring has a C5-envelope conformation, with an elongated C_{sp^3}—C_{sp^3} bond length of 1.569 (2) Å. One hydroxyl group takes part in a bifurcated hydrogen bond involving an intra- and intermolecular bond to adjacent hydroxyl

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† Present address: Center for Macromolecular Crystallography, University of Alabama, THT-79, Birmingham, AL 35294-0005, USA.