are reasonably close to the ideal *skew* (s^+, s^- or $\pm 120°$) conformations.

The conformation of the *R*C(=O)—NHOH moiety is synperiplanar (Kjøller Larsen, 1988). The O(3)···O(4) *intra*molecular distance [2.703 (3) Å] is in the range suitable for O—H···O bonding, but this is not observed. Rather, the O—H bond is part of the *inter*molecular hydrogen-bonding scheme (see below).

The crystal packing of the Z-Ac$_3$c-NHOH molecules is characterized by three intermolecular hydrogen bonds between: (i) the hydroxamic acid O(4)—H and O(3)=C(12) groups of symmetry-related ($-x$, $2-y$, $2-z$) molecules; (ii) the hydroxamic acid N(2)—H and urethane O(2)=C(8) groups of symmetry-related ($-x$, $1-y$, $1-z$) molecules; and (iii) the urethane N(1)—H group and the hydroxamic acid O(4) atom of symmetry-related (x, $y-1$, z) molecules. The O(4)···O(3) separation is 2.620 (3) Å, whereas the N(2)···O(2) and N(1)···O(4) distances are 2.806 (3) and 3.060 (3) Å, respectively.

References

ALLEN, F. H. (1981). *Acta Cryst.* B**37**, 890–900.

BENEDETTI, E. (1982). *Chemistry and Biochemistry of Amino Acids, Peptides and Proteins*, Vol. 6, edited by B. WEINSTEIN, pp. 105–184. New York: Dekker.

BENEDETTI, E., DI BLASIO, B., PAVONE, V., PEDONE, C., SANTINI, A., CRISMA, M., VALLE, G. & TONIOLO, C. (1989). *Biopolymers*, **28**, 175–184.

BENEDETTI, E., PEDONE, C., TONIOLO, C., DUDEK, M., NÉMETHY, G. & SCHERAGA, H. A. (1983). *Int. J. Pept. Protein Res.* **21**, 163–181.

BENEDETTI, E., PEDONE, C., TONIOLO, C., NÉMETHY, G., POTTLE, M. S. & SCHERAGA, H. A. (1980). *Int. J. Pept. Protein Res.* **16**, 156–172.

BRECKENRIDGE, R. J. & SUCKLING, C. J. (1986). *Tetrahedron*, **42**, 5665–5677.

CHIMIAK, A. & MILEWSKA, M. J. (1988). *Progress in the Chemistry of Organic Natural Compounds*, Vol. 53, edited by W. HERZ, H. GRISEBACH, G. W. KIRBY & C. TAMM, pp. 203–277. Wien: Springer.

HOLMES, M. A. & MATTHEWS, B. W. (1981). *Biochemistry*, **20**, 6912–6920.

KJØLLER LARSEN, I. (1988). *Acta Cryst.* B**44**, 527–533.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN*78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

NISHINO, N. & POWERS, J. C. (1978). *Biochemistry*, **17**, 2846–2850.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SUCKLING, C. J. (1986). *Biochem. Soc. Trans.* pp. 402–404.

SUCKLING, C. J. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 537–552.

TONIOLO, C. & BENEDETTI, E. (1988). *ISI Atlas of Science: Biochemistry*, Vol. 1, pp. 225–230.

VALLE, G., FORMAGGIO, F., CRISMA, M., TONIOLO, C., BOESTEN, W. H. J., POLINELLI, S., SCHOEMAKER, H. E. & KAMPHUIS, J. (1992). *Z. Kristallogr.* In the press.

ZIMMERMAN, S. S., POTTLE, M. S., NÉMETHY, G. & SCHERAGA, H. A. (1977). *Macromolecules*, **10**, 1–9.

Acta Cryst. (1992). C**48**, 1466–1471

Structure of the (1:1:1) Complex 2*a*,2*b*,2*c*,2*d*,2*e*,2*f*,3*a*,3*g*,6*a*,6*b*,6*c*,6*d*,6*e*,6*f*,6*g*-Pentadeca-*O*-methyl-β-cyclodextrin–1,7-Dioxaspiro[5.5]undecane–Methanol

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Abstract. $C_{67}H_{120}O_{38}$, $M_r = 1533.66$, triclinic, $P1$, $a = 10.673$ (3), $b = 15.776$ (3), $c = 16.103$ (4) Å, $\alpha = 122.77$ (2), $\beta = 110.09$ (2), $\gamma = 68.13$ (2)°, $V = 2080$ Å^3, $Z = 1$, $D_x = 1.20$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54056 Å, $\mu = 8.10$ cm^{-1}, $F(000) = 826$, $T = 293$ K, final $R = 0.078$ for 6294 reflections. The study of the title methylated cyclodextrin molecule reveals an over-methylation on one residue coupled with an O(2)–O(3) permutated methylation on the neighbouring residue. The important dissymmetry of the host molecule leads to chiral discrimination of the dioxaspiro[5.5]undecane 'guest' molecule, yielding a complex of only the *S* enantiomer which is completely enclosed in the cyclodextrin cavity.

Introduction. Cyclodextrins (CD's), cyclic oligosaccharides having α(1–4) linked glucose units, are formed by the enzymatic degradation of amylose and are well documented for their ability to form inclusion complexes with a wide variety of 'guest' molecules (Szetjli, 1989). Many studies of crystal structures of CD complexes have been reported (Saenger, 1980; Le Bas & Rysanek, 1987). Methylated CD (MCD) complexes have already been stu-

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died, particularly trimethylated CD complexes in which all the hydroxyl groups are replaced by methyl groups (Harata, Uekama, Otagiri & Hirayama, 1984; Harata, 1990). In view of the modulation of inclusion properties by methylation, it appeared interesting to investigate the crystal structure of a dimethyl β-CD (DM β-CD, β-CD = seven glucose units) complex in which only the secondary O(2) hydroxyl groups and all the primary O(6) hydroxyl groups are replaced by methyl groups, with the O(3) hydroxyl groups remaining free (Fig. 1). Very few structural studies of such compounds have been published (Czugler, Eckle & Stezowski, 1981; Harata, 1988; Harata, Hirayama, Uekama & Tsoucaris, 1988).

The chosen 'guest' was the synthetic racemate of (*R*)- and (*S*)-1,7-dioxaspiro[5.5]undecane, which constitutes the major component of the olive fruit fly (*Dacus oleae*) pheromone (Baker, Herbert, Howse, Jones, Francke & Reith, 1980). It is a volatile liquid at normal temperature and its crystal structure has not been determined, to our knowledge. The use of crystalline CD complexes presents a way of obtaining structural information about such molecules. Several attempts at the use of inclusion complex formation with the, by definition, chiral cyclodextrins for racemic resolution and chiral recognition have been performed, in the liquid phase (Armstrong, 1984) as well as in the solid phase (Harata, Uekama, Otagiri & Hirayama, 1984). Such discrimination appears to be favoured for the less symmetric methylated CD's with their higher degree of conformational adaptability (Harata, Uekama, Otagiri & Hirayama, 1984). However, a recent example of a structural determination of an inclusion complex of β-cyclodextrin with racemic fenoprofen shows direct evidence of chiral recognition (Hamilton & Chen, 1988). Hence this present study was also undertaken to try to assess the enantiomeric separation of the 'guest' molecule.

Finally, a practical interest concerns the evaluation of DM β-CD as a potential slow-release system for the olive fruit fly sex pheromone.

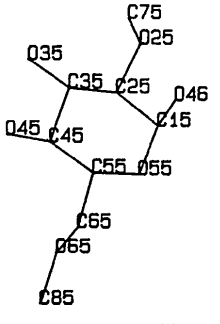

Fig. 1. View of a 2,6-methylglucose residue with atom numbering. The last number is the residue number (residue 5 is shown).

Table 1. *X-ray data collection and structure refinement*

Scan type	ω–2θ
θ range, data collection (°)	2–65
Range of initial *hkl* indices	$-12 < h < 12$, $0 < k < 18$, $-18 < l < 18$
R_{int}	0.048
Number of reflections measured	7342
Number of unique reflections	6823
Number of reflections with $I > 3\sigma(I)$	6294
Number of parameters refined	964
Weight, w	$1/[\sigma^2(F_o) + gF_o^2]$, $g = 0.014$
Largest peaks in the final difference Fourier maps (e Å^{-3})	0.32, −0.34
S	0.969
R	0.078
wR	0.087

Experimental. The crystal was obtained by slow evaporation from a methanolic dioxaspiroundecane/DM β-CD solution. A colourless plate crystal approximately 0.5 × 0.5 × 0.05 mm, sealed in a glass capillary was tested by photographic methods and mounted on an Enraf–Nonius CAD-4 diffractometer (graphite-monochromated Cu $K\alpha$ radiation). Cell constants were obtained from setting angles of 25 reflections in the range $8 < \theta < 35°$. Details of data collection and structure refinement are given in Table 1.

Three standard reflections ($\bar{1}2\bar{6}$, $\bar{3}12$, $\bar{1}3\bar{6}$) showed a 5.5% average decrease of intensity during 116 h of data collection; a decay correction was applied. Data were corrected for Lorentz and polarization effects; empirical absorption corrections using the *DIFABS* program (Walker & Stuart, 1983) were applied after isotropic convergence; maximum and minimum correction factors 1.4 and −0.8. Atomic scattering factors were taken from *SHELX*76 program (Sheldrick, 1976). *F* magnitudes were used in the least-squares refinements.

The structure was resolved using the rotation function (Navaza, 1987, 1990) with a set of coordinates of a published structure from which the primary hydroxyl groups had been removed (Harata, 1982). Most calculations were carried out using the *SHELX*76 program (Sheldrick, 1976) on a VAX computer; some calculations used the *SDP* programs (Enraf–Nonius, 1988). Successive full-matrix least-squares refinements and difference Fourier syntheses were performed. All non-H atoms were refined anisotropically, except the O atom O(63) present in disordered positions, some C methyl atoms with high equivalent temperature factors and the solvent molecules. H atoms were introduced at calculated non-refined positions except for some hydroxyl group H atoms which were found in difference Fourier maps. CH_3 moieties were treated as rigid groups. Refinements were in three blocks. Final agreement factors $R = 0.078$, $wR = 0.087$. This is a good R value for a cyclodextrin structure; usually cyclodextrin structure refinements give relatively high R values because of the size and the great flexibility of

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

In the table an asterisk indicates atoms refined anisotropically; $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{iso}/U_{eq}		x	y	z	U_{iso}/U_{eq}
O(41)†	646	3752	1876	76 (6)*	O(45)	24 (3)	−3082 (2)	−2663 (2)	73 (6)*
C(11)	−1031 (6)	4190 (4)	4094 (4)	99 (9)*	C(15)	1251 (6)	−1962 (4)	−3982 (4)	92 (9)*
C(21)	−1988 (6)	4623 (5)	3383 (5)	118 (11)*	C(25)	7 (6)	−2436 (4)	−4563 (4)	80 (9)*
C(31)	−1356 (6)	4098 (4)	2444 (4)	92 (10)*	C(35)	−558 (6)	−2528 (4)	−3873 (4)	78 (9)*
C(41)	75 (6)	4282 (4)	2758 (3)	69 (9)*	C(45)	596 (5)	−3108 (4)	−3364 (4)	74 (8)*
C(51)	941 (6)	3871 (4)	3498 (4)	89 (9)*	C(55)	1794 (5)	−2585 (4)	−2814 (4)	78 (9)*
C(61)	2335 (7)	4065 (5)	3884 (4)	131 (12)*	C(65)	3015 (5)	−3153 (4)	−2341 (4)	84 (10)*
C(71)	−4431 (11)	5248 (9)	3075 (9)	98 (3)	C(75)	−1693 (10)	−2292 (7)	−5957 (6)	141 (18)*
C(81)	3557 (7)	5365 (7)	4662 (6)	132 (14)*	C(85)	4479 (8)	−4762 (6)	−2610 (7)	148 (16)*
C(331)	−2923 (9)	3775 (8)	877 (7)	174 (20)*	O(25)	−985 (5)	−1816 (3)	−4990 (3)	97 (8)*
O(21)	−3295 (5)	4447 (5)	3150 (4)	200 (12)*	O(35)	−1635 (5)	−3050 (3)	−4448 (3)	91 (8)*
O(31)	−2202 (5)	4490 (4)	1773 (3)	134 (9)*	O(55)	2252 (3)	−2517 (3)	−3525 (3)	92 (6)*
O(51)	277 (4)	4354 (3)	4348 (3)	84 (7)*	O(65)	3397 (5)	−4210 (3)	−3055 (3)	108 (8)*
O(61)	2255 (5)	5133 (3)	4246 (3)	86 (8)*	O(46)	783 (3)	−919 (3)	−3282 (3)	76 (6)*
O(42)	−991 (4)	3128 (3)	3621 (2)	83 (6)*	C(16)	1317 (5)	1996 (4)	−2153 (4)	95 (9)*
C(12)	−1198 (5)	864 (4)	4065 (4)	98 (9)*	C(26)	168 (6)	1673 (4)	−3044 (4)	89 (9)*
C(22)	−2475 (5)	1748 (5)	4189 (4)	99 (10)*	C(36)	−148 (5)	719 (4)	−3211 (4)	87 (8)*
C(32)	−2410 (6)	2363 (4)	3735 (4)	91 (9)*	C(46)	1154 (5)	−134 (4)	−3279 (4)	68 (8)*
C(42)	−1083 (5)	2708 (4)	4187 (3)	88 (9)*	C(56)	2297 (6)	271 (4)	−2377 (4)	80 (10)*
C(52)	160 (5)	1811 (4)	4138 (4)	84 (9)*	C(66)	3665 (10)	−516 (7)	−2467 (8)	119 (21)*
C(62)	1463 (7)	2180 (5)	4708 (5)	113 (12)*	C(76)	−965 (9)	3279 (5)	−3009 (5)	121 (14)*
C(72)	−4664 (11)	1744 (12)	4222 (11)	195 (33)*	C(86)	5251 (19)	−1685 (15)	−3533 (15)	163 (6)
C(82)	2496 (13)	3319 (7)	6262 (8)	123 (24)*	O(26)	−1060 (5)	2437 (3)	−2950 (3)	110 (8)*
O(22)	−3662 (4)	1317 (4)	3701 (4)	106 (9)*	O(36)	−1115 (5)	367 (3)	−4115 (3)	90 (8)*
O(32)	−3560 (5)	3223 (3)	3896 (4)	132 (10)*	O(56)	2496 (4)	1166 (3)	−2306 (3)	80 (7)*
O(52)	−25 (4)	1272 (3)	4551 (3)	94 (7)*	O(66)	4000 (8)	−919 (5)	−3407 (7)	197 (19)*
O(62)	1325 (6)	2933 (4)	5707 (4)	106 (10)*	O(47)	870 (3)	2329 (3)	−1263 (2)	70 (6)*
O(43)	−1203 (4)	201 (3)	3032 (2)	82 (6)*	C(17)	1351 (6)	4315 (4)	1790 (4)	81 (9)*
C(13)	−700 (5)	−2868 (4)	848 (4)	93 (9)*	C(27)	413 (6)	4793 (4)	1130 (4)	83 (9)*
C(23)	−2035 (5)	−2364 (4)	1250 (4)	86 (10)*	C(37)	61 (5)	3957 (4)	50 (4)	83 (9)*
C(33)	−2248 (5)	−1206 (4)	1846 (4)	83 (9)*	C(47)	1329 (5)	3178 (4)	−355 (3)	64 (8)*
C(43)	−982 (5)	−893 (4)	2640 (4)	86 (9)*	C(57)	2268 (6)	2778 (4)	389 (4)	93 (10)*
C(53)	287 (6)	−1449 (4)	2162 (4)	91 (11)*	C(67)	3664 (9)	2144 (6)	98 (5)	164 (17)*
C(63)	1606 (9)	−1248 (7)	2941 (6)	139 (17)*	C(337)	−2083 (8)	4508 (6)	−846 (6)	153 (15)*
C(73)	−4199 (8)	−2825 (8)	576 (9)	107 (19)*	C(87)	5132 (16)	1789 (13)	1408 (12)	142 (4)
C(83)	3985 (20)	−1405 (16)	3124 (15)	142 (6)	O(27)	−781 (5)	5515 (3)	1541 (3)	108 (8)*
O(23)	−3118 (4)	−2680 (4)	409 (4)	88 (8)*	O(37)	−668 (4)	4431 (3)	−573 (3)	115 (8)*
O(33)	−3407 (4)	−791 (4)	2326 (4)	98 (9)*	O(57)	2515 (4)	3629 (3)	1382 (3)	102 (7)*
O(53)	403 (4)	−2558 (3)	1638 (3)	104 (7)*	O(67)	4317 (8)	1446 (6)	459 (6)	118 (2)*
O(63*A*)	2680 (11)	−1567 (8)	2497 (8)	104 (4)	C(*P*)	81 (10)	278 (6)	354 (6)	143 (16)*
O(63*B*)	1707 (23)	−1496 (18)	3614 (18)	97 (8)	O(*P*1)	−162 (7)	1076 (4)	137 (4)	139 (12)*
O(44)	−819 (3)	−2584 (2)	114 (2)	80 (6)*	C(*P*1)	−659 (14)	789 (9)	−882 (7)	195 (25)*
C(14)	186 (5)	−4026 (4)	−2693 (4)	70 (8)*	C(*P*2)	−2001 (14)	536 (9)	−1205 (9)	209 (27)*
C(24)	−1187 (5)	−4077 (4)	−2656 (4)	69 (9)*	C(*P*3)	−1888 (16)	−360 (10)	−1056 (10)	182 (31)*
C(34)	−1576 (5)	−3285 (4)	−1641 (4)	81 (9)*	C(*P*4)	−1238 (13)	−93 (10)	60 (10)	175 (27)*
C(44)	−415 (5)	−3404 (3)	−821 (4)	80 (8)*	O(*PP*)	1016 (8)	−613 (4)	−184 (4)	133 (13)*
C(54)	902 (5)	−3343 (4)	−933 (4)	88 (9)*	C(*PP*1)	2312 (18)	−490 (10)	9 (8)	193 (30)*
C(64)	2125 (6)	−3472 (5)	−160 (5)	133 (12)*	C(*PP*2)	2970 (19)	−99 (12)	1131 (11)	179 (38)*
C(74)	−3308 (6)	−4357 (6)	−3833 (5)	104 (12)*	C(*PP*3)	2009 (16)	883 (9)	1750 (9)	146 (29)*
C(84)	3319 (11)	−4443 (9)	681 (8)	100 (3)	C(*PP*4)	609 (14)	734 (8)	1485 (7)	192 (23)*
O(24)	−2143 (4)	−3927 (3)	−3461 (3)	95 (8)*	O(*M*1)	−3795 (23)	1426 (18)	−3635 (18)	172 (6)
O(34)	−2802 (4)	−3428 (4)	−1594 (3)	113 (8)*	C(*M*1)	−4331 (36)	466 (27)	−3971 (28)	171 (10)
O(54)	1198 (4)	−4132 (3)	−1904 (3)	96 (7)*	O(*M*2)	−4454 (23)	3130 (18)	−1699 (18)	180 (6)
O(64)	2268 (6)	−4365 (4)	−105 (4)	162 (11)*	C(*M*2)	−5439 (36)	2983 (28)	−1422 (28)	148 (10)

† The *x*, *y*, *z* coordinates of atom O(41) were fixed to define the origin for the non-centrosymmetric structure.

the molecule (Hamilton & Chen, 1988). Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2.* Graphics visualization of the structure shows the unit cell reported in the *Abstract*, to allow an easier interpretation of the molecular packing.

Data collection and refinements were performed with a different initial cell: $a = 10.673$ (3), $b = 15.406$ (3), $c = 15.974$ (4) Å, $\alpha = 121.80$ (2), $\beta = 71.12$ (2), $\gamma = 108.14$ (2)°. The transformation matrix 100, 110, −101 was then applied to yield the descriptive unit.

Discussion. *MCD macrocycle.* This crystal structure reveals unexpected results concerning the host molecule MCD, clearly showing that an overmethylation occurs relative to the expected 2,6-*O*-methyl β-CD. The glycosidic residue labelled *A* in Fig. 2 (number 1) is totally methylated at the O(2), O(3) and O(6) atoms. Moreover, the neighbouring residue labelled *G* (number 7) is methylated at the O(3) atom instead of the O(2) atom as well as at the O(6) atom. The remaining five rings are 2,6-methylated (Fig. 2). It may be that the occurrence of such a substitution pattern at adjacent

* Lists of structure factors, anisotropic thermal parameters bond distances and angles, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55069 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0255]

positions is not a simple coincidence; however, its chemical and stereochemical significance are not understood at present. An over-methylation has already been observed in the liquid phase (Spencer, Stoddart & Zarzycki, 1987). As noted by the authors, any non-symmetric modification of a CD leads to a totally dissymetric molecule. Harata (1990) observed the existence of one additional methyl group linked at O(3) in 2,6-dimethyl-α-cyclodextrin, removing its approximate sixfold axis.

As is usual in CD's, the MCD molecule almost has the shape of a truncated cone. The macrocycle ring is slightly distorted relative to a pseudo-sevenfold axis; a pseudo-heptagon is formed by the seven O4 atoms; the distances from the O(4) atoms to the centre of the heptagon are 4.621 (1), 5.017 (3), 5.383 (3), 5.073 (3), 4.911 (2), 5.043 (4) and 5.184 (4) Å for O(41)–O(47) respectively. The distances O(4n)—O(4n + 1) range between 4.261 (5) and 4.457 (4) Å. The seven O(4) atoms are approximately located in a plane, the distances to the least-squares plane range between 0.37 to −0.31 Å. The glycosidic O atom angles C(1n + 1)—O(4n)—C(4n) range between 116.9 and 119.8°. All these values are very close to those usually observed in most CD and methylated CD complexes (Harata, Uekama, Otagiri & Hirayama, 1984).

There are only six intramolecular hydrogen bonds between O(2n) and O(3n + 1) atoms of the neighbouring residue (Fig. 2) which stabilize the macrocycle; atoms O(26) and O(37) are both linked to methyl groups with a normal 3.40 (1) Å van der Waals distance between them, while the neighbouring methyl groups, C(76)–C(337), are 3.34 (2) Å apart.

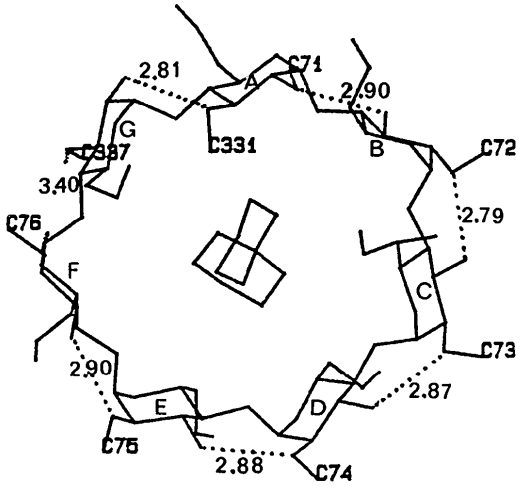

Fig. 2. View of the MCD macrocycle from the secondary side. The methyl C atoms on the secondary side are labelled. O(2)—O(3) distances are indicated. Dashed lines represent hydrogen bonds.

Table 3. *Tilt angles* (°) *and torsion angles* (°)

	*G*1	*G*2	*G*3	*G*4	*G*5	*G*6	*G*7
Tilt angle	−13.1	9.9	18.5	16.0	18.5	7.7	22.3
C(4)—C(5)—C(6)—O(6)	50.5	55.3	−167.4	50.9	51.3	50.6	−155.2
O(5)—C(5)—C(6)—O(6)	−71.5	−66.1	55.4 72.7	−70.5	−69.4	−69.4	83.5
C(5)—C(6)—O(6)—C(8)	177.4	−178.6	−64.5 178.1	−174.0	−176.4	−178.0	−88.0

The ability of a methylated CD molecule to adopt an optimal conformation is related to the value of the inclination of the residues relative to the molecular axis or tilt angle. This is measured by the angle between plane C(1n), C(4n), O(4n), O(4n + 1) and the plane of O(4) (Table 3). It is interesting to note the opposite sense of the tilt angle for residue *G*7 (22.3°) and for consecutive residue *G*1 (−13.1°). In most CD molecules and derivatives, the tilt angle is such that the primary side is closer to the molecular axis than the secondary one. This confers the usual 'trapezoid form' to the molecules with the residues 'tilted in'. But in the present structure, the over-methylated residue *G*1 is 'tilted out', *i.e.*, the primary side is more distant from the sevenfold axis than the secondary one. As is usual in CD, the torsion angles concerning the orientation of the C(6)—O(6) bonds show two types of conformation; *gauche–trans* for residues *G*3 and *G*7 and *gauche–gauche* for the other residues (Table 3). From the values of the torsion angle C(5)—C(6)—O(6)—C(8), the C(8)—O(6) bonds are *trans* relative to the C(50—C(6) bonds except for the *G*1, *G*3, *G*6 residues; the *G*7 residue shows a particularly small torsion angle. We observe disorder of the O(63) atom which is a normal occurrence for O(6) atoms in β-CD structures.

On the secondary side, the six O(2)—C(7) bonds all point away from the centre of the macrocyclic ring. A similar orientation has been observed by Harata, Uekama, Otagiri & Hirayama (1984). In contrast, the O(31)—C(331) and O(37)—C(337) bonds (those with the two 'special' methyl groups) are oriented toward the centre. This fact, together with the 'tilt out' conformation of *G*1, brings the C(331) methyl closer to the centroid axis [3.17 (1) Å] and in close contact with the pheromone 'guest' molecule; C(331)—O(*P*1) = 3.97 (1) Å. The O(2)—C(7) bond is nearly *gauche* relative to the C(1)—C(2) bond in the residue *G*6 with C(1)—C(2)—O(2)—C(7) = 70.3°; for the five other residues the average torsion angle is 142.5°. The only solvent sites are *M*(1) and *M*(2), with an occupation factor of 0.5. They have hydrogen bonds between themselves and between *M*(1) and the O(36) atom of the MCD molecule: O(36)···O(*M*1) = 2.85 (3), O(*M*1)···O(*M*2) = 2.91 (4) Å.

Molecular packing. The structure shows monomers of methyl cyclodextrin (MCD) completely enclosing

the dioxaspiro[5.5]undecane molecule (Fig. 3). Unlike most of the *P*1 structures encountered in β-CD compounds, the crystallographic unit cell comprises only one macrocycle. The packing is characterized by infinite layers of MCD molecules; the distance between layers is 8.63 Å and the average planes of the molecules [O(4) plane] are inclined at an angle of 12.36° relative to the crystallographic *bc* plane. The MCD cavity is partially closed by the neighbouring MCD molecules of the following layer. The shift between molecules in successive layers is 6.28 Å, roughly the width of half a molecule. Table 4 gives the distances less than 4 Å between MCD molecules. The methanol solvent molecules occupy interlayer spaces.

Guest molecule. The structure reveals that the pheromone 'guest' molecule is clearly located inside the macrocycle of the MCD molecule. The distance between the centres of the two molecules is 0.35 Å. It is remarkable that in the very first Fourier difference maps, the intensity of the peaks corresponding to the atoms of the guest molecule were higher than those for most C-methyl atoms of the MCD molecule. The positions of the two O atoms of the pheromone are localized without ambiguity, from the shorter values of C—O distances between peaks. Only the *S* enantiomer is present in the cavity. The chirality of the pheromone arises from the *C*2 symmetry through the central C atom. Even with the relatively high thermal motion of the 'guest', which is a common fact in CD complexes, and which is in the same range as that of some methyl C atoms of MCD, we may state that only the *S* enantiomer is present. The height of the first peak in the last Fourier difference map is 0.3 e $Å^{-3}$ and the other enantiomer cannot be localized on the map.

Distances of the dioxaspiro[5.5]undecane molecule determined by a non-constrained refinement are given in Fig. 4. No hydrogen bonds are observed between the host and the guest molecules, but numerous van der Waals contacts (Table 5) assure the tightness of the host–guest fit. Each atom of the pheromone molecule [except the C(*P*) central atom and the C(*P*2) atom] have van der Waals contacts with the MCD molecule. These contacts involve O(4), C(5) and O(6) atoms on the primary side; there is one contact on the secondary side with C(36) and with the additional methyl group C(331) which seems important for the chiral recognition. One other van der Waals contact is observed with the *x*-translated MCD molecule.

It is remarkable that in spite of the absence of strong bonds between the host and the guest molecule, the presence of numerous van der Waals contacts and the dissymmetry of the host molecule are sufficient to cause an efficient enantiomeric discrimination.

We thank Dr Mazomenos for providing the sample of pheromone, Dr Tsomi for the preparation of the inclusion complex, Professor Galons for the synthesis of MCD and Dr De Rango for helpful discussions.

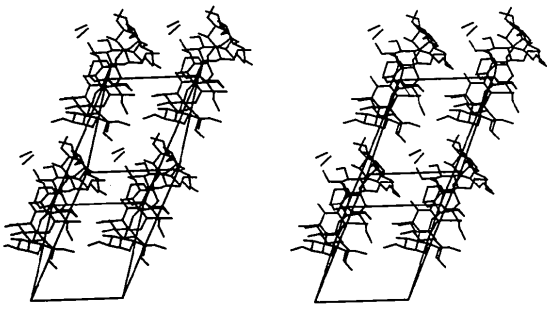

Fig. 3. Stereo packing diagram showing MCD molecular layers.

Table 4. *van der Waals contacts* (Å) *between MCD molecules*

C(81)···O(32^{i})	3.57 (1)	C(84^{iii})···C(71)	3.96 (2)
C(85^{ii})···O(34)	3.62 (1)	C(84^{iii})···C(331)	3.97 (2)
C(85^{ii})···C(74)	3.94 (1)	C(85)···C(337^{iv})	4.01 (2)
C(86^{ii})···O(35)	3.53 (2)	C(73)···C(337^{vi})	3.75 (1)
C(86^{ii})···C(74)	3.72 (2)	O(34)···C(337^{vi})	3.79 (1)
C(73)···C(337^{vi})	3.75 (1)	C(81)···C(74^{v}i^{ii})	3.41 (1)
C(87^{ii})···O(32)	3.44 (1)	O(32)···C(74^{v})	3.604 (7)
C(81^{ii})···C(71)	3.76 (1)		

Symmetry code: (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $x-1, y+1, z$; (iv) $x+1, y-1, z$; (v) $x, y+1, z+1$; (vi) $x, y+1, z$; (vii) $x+1, y+1, z+1$.

Table 5. *Distances* (*less than* 4 Å) *between the pheromone molecule and the MCD molecule in the same unit cell*

O(*P*1)—C(331)	3.97 (1)	O(*PP*)—C(54)	3.83 (1)
O(*P*1)—O(41)	3.83 (1)	O(*PP*)—O(45)	3.945 (5)
C(*P*1)—O(46)	3.78 (1)	O(*PP*)—C(55)	3.812 (6)
C(*P*1)—C(36)	3.91 (1)	C(*PP*1)—C(55)	3.91 (1)
C(*P*1)—O(47)	3.77 (1)	C(*PP*1)—C(65)	3.86 (1)
C(*P*3)—O(45)	3.79 (1)	C(*PP*1)—O(67)	3.979 (17)
C(*P*4)—O(44)	3.83 (1)	C(*PP*2)—O(67)	3.96 (2)
		C(*PP*2)—O(67)	3.96 (2)
C(*PP*2)—O(33^{i})	3.72 (1)	C(*PP*3)—C(51)	3.91 (1)
		C(*PP*4)—O(42)	3.76 (1)
		C(*PP*4)—C(52)	3.78 (1)

Symmetry code: (i) $x+1, y, z$.

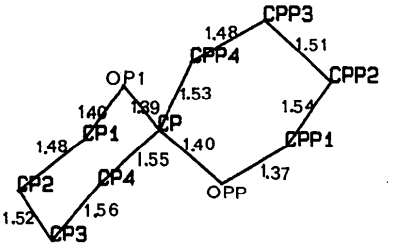

Fig. 4. View of the 1,7-dioxaspiro[5.5]undecane molecule.

References

ARMSTRONG, D. W. (1984). *J. Liq. Chromatogr.* **7**(S2), 353–376.
BAKER, R., HERBERT, R., HOWSE, P. E., JONES, O. T., FRANCKE, W. & REITH, W. (1980). *J. Chem. Soc. Chem. Commun.* pp. 52–53.
CZUGLER, M., ECKLE, E. & STEZOWSKI, J. (1981). *J. Chem. Soc. Chem. Commun.* pp. 1291–1292.
Enraf–Nonius (1988). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
HAMILTON, J. A. & CHEN, L. (1988). *J. Am. Chem. Soc.* **110**, 4379–4391, 5833–5841.
HARATA, K. (1982). *Bull. Chem. Soc. Jpn*, **55**, 2315–2320.
HARATA, K. (1988). *Bull. Chem. Soc. Jpn*, **61**, 1939–1944.
HARATA, K. (1990). Minutes. 5th Int. Symp. Cyclodextrins, Paris.
HARATA, K., HIRAYAMA, F., UEKAMA, K. & TSOUCARIS, G. (1988). *Chem. Lett.* pp. 1585–1588.
HARATA, K., UEKAMA, K., OTAGIRI, M. & HIRAYAMA, F. (1984). *J. Incl. Phenom.* **1**, 279–293; **2**, 583–594.
LE BAS, G. & RYSANEK, N. (1987). *Cyclodextrins and Their Industrial Uses*, ch. III, edited by D. DUCHENE, p. 105. Paris: Editions de Santé.
NAVAZA, J. (1987). *Acta Cryst.* A**43**, 645–653.
NAVAZA, J. (1990). *Acta Cryst.* A**46**, 619–620.
SAENGER, W. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 344–362.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SPENCER, C. M., STODDART, J. F. & ZARZYCKI, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. 1323–1336.
SZETJLI, J. (1989). *Cyclodextrin Technology*. Dordrecht: Kluwer Academic Publishers.
WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1992). C**48**, 1471–1474

Mesoionic Compounds. 3.* Structure of the Hydrochloride of 5-(4-Methoxyphenyl)-4-phenyl-1,3,4-thiadiazolium-2-phenylaminide

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Abstract. 5-(4-Methoxyphenyl)-4-phenyl-2-phenylamino-1,3,4-thiadiazolium chloride, $C_{21}H_{18}N_3OS^+.Cl^-$, $M_r = 395.91$, orthorhombic, *Pbca*, $a = 15.809\ (4)$, $b = 12.207\ (2)$, $c = 19.772\ (5)$ Å, $V = 3815.5\ (1.4)$ Å^3, $Z = 8$, $D_x = 1.378$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 3.2$ cm^{-1}, $F(000) = 1648$, $T = 297$ K, $R = 0.041$ for 1159 reflections with $|F_o| > 2\sigma(|F_o|)$. The pentatomic ring has two conjugated systems separated by S—C and N—N single bonds.

Introduction. The concept of mesoionic compounds has developed gradually, undergoing a number of

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