Synthesis and Crystal Structures of Normethyl Analogues of Dianin's Compound

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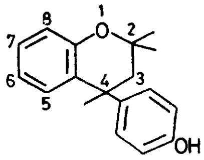
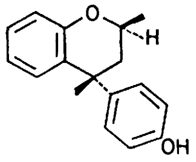
As part of a study of inclusion behaviour, chromans (II) and (III) have been prepared, normethyl analogues of the versatile host Dianin's compound (I). Compound (II), which lacks the 2-methyl group *cis* to the *p*-hydroxyphenyl substituent, retains the ability to form clathrates. Crystals of the carbon tetrachloride clathrate of (II) are trigonal, space group $R\bar{3}$, with a = 26.936(6), c = 10.796(1) Å, and 18 host and 3 guest molecules in the hexagonal unit cell. An *X*-ray study has shown that the new cavity-shape is markedly different from that of the parent (I). In contrast to (II), the 4-nor-analogue (III) crystallises unsolvated in the tetragonal system, space group $P\bar{4}2_1c$, with a = 12.640(2), c = 17.254(4) Å, and Z = 8. This structure has infinite chains of molecules linked head-to-tail by O–H · · · O hydrogen bonds of length 2.82(1) Å.

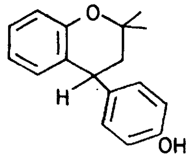
A FUNDAMENTAL aspect of the study of clathrate inclusion compounds is the design and synthesis of new hosts with controlled-cavity geometry.[1] Efficient control of the steric environment in which a guest species is situated is of interest with respect to spectroscopic and reactivity studies, and also has an important bearing on selective clathration from solvent mixtures. The present study concerns clathrate engineering of a known host with a view to producing a new host with a significantly modified cavity geometry. The starting molecule, Dianin's compound (I), forms clathrates in which the guest molecules are accommodated in hour-glass shaped cavities.[2] In the present work [3] we describe the successful elimination of the central constriction in the cage of (I), the modified cage geometry being defined by *X*-ray methods. The new host (II), which lacks the 2-methyl group *syn* to the *p*-hydroxyphenyl substituent of (I), was prepared by the action of anhydrous hydrogen chloride on a mixture of phenol and pent-3-en-2-one. Independent work [4] has recently established that 4-*p*-hydroxyphenyl-*trans*-2,4-dimethylchroman, the C-2 epimer of (II), also possesses host properties. We also describe the synthesis and *X*-ray structure of the 4-normethyl analogue (III) which forms unsolvated tetragonal crystals.



(I)



(II)
(and enantiomer)



(III)

EXPERIMENTAL

Preparation of 4-p-*Hydroxyphenyl*-cis-2,4-*dimethylchroman*, (II).—A mixture of phenol (67.1 g) and pent-3-en-2-one (15.0 g) was saturated (6 h) at 0 °C with anhydrous HCl. The resulting black viscous liquid was set aside in an oven at 45 °C for 4 days. The excess of phenol was removed by extraction with boiling water, when a gum remained which did not crystallise on addition of ethanol; chromatography on Mallinckrodt silicic acid (ratio 25 : 1, elution with 50% ethyl acetate in benzene) yielded a black oil which solidified on introduction of ethanol. Recrystallisation from benzene gave brown prisms which required sublimation (110 °C/0.01 mmHg) for decolourisation. A ^{1}H n.m.r. spectrum of the sublimed material showed it to be a mixture of (II) and Dianin's compound (I), the separation of which was accomplished by gel chromatography (200 × 2.5 cm column of Sephadez LH 20 modified [5] with Nedox 1114, elution with methanol, s.e.v. *ca.* 100). Recrystallisation from carbon tetrachloride gave an adduct, m.p. 156—160 °C, for which a host : guest ratio of 6 : 1 was found by microanalysis (Found: C, 73.85; H, 6.5; Cl, 8.3. $C_{17}H_{18}O_2\cdot\frac{1}{6}CCl_4$ requires C, 73.64; H, 6.48; Cl, 8.44%; *M*, 254); *m/e* 254 (M^+); $\nu_{max.}$(KBr) 3 275 cm^{-1} (OH); τ(CDCl$_3$) 8.74 (3 H, d, *J* 6.5 Hz), 8.30 (3 H, s), *ca.* 8.0 (2 H, m, diastereotopic CH$_2$), 6.15 (1 H, m), 5.2 (1 H, s, OH), and *ca.* 2.7—3.4 (8 H, partially overlapping ArH ABCD and XX′YY′ systems).

On recrystallisation from cyclohexane, (II) gave an adduct with a host : guest ratio of 5 : 1 (determined by ^{1}H n.m.r.).

Preparation of 4-p-*Hydroxyphenyl*-2,2-*dimethylchroman*, (III).—A mixture of phenol (18 g) and 2,2-dimethyl-2*H*-chromen [6] (14 g) was saturated with anhydrous HCl for 2 h at 0 °C. The resulting mixture was set aside (CaCl$_2$ tube) for 14 days at ambient temperature. The red-brown viscous oil produced was extracted with boiling water (6 × 200 ml) to remove excess of phenol. Hot methanol was added to the oil, and after this was set aside overnight, a crystalline product consisting mainly of (III) was deposited. Repeated recrystallisations from methanol gave pure (III) as unsolvated crystals, m.p. 143.5—144 °C (Found: C, 80.3; H, 7.1. $C_{17}H_{18}O_2$ requires C, 80.31; H, 7.08%; *M* 254); *m/e* 254 (M^+); $\nu_{max.}$(KBr) 3 355 cm^{-1} (OH); τ(CDCl$_3$) 8.67, 8.57 (each 3 H, s), *ca.* 8.0 (2 H, m, diastereotopic CH$_2$), 5.97 (1 H, m), 5.2 (1 H, s, OH), and *ca.* 2.8—3.4 (8 H, overlapping ArH ABCD and XX′YY′ systems).

Compound (III) also crystallises unsolvated from acetic acid, cyclohexane, and carbon tetrachloride.

Crystal Data for (II).—$C_{17}H_{18}O_2\cdot\frac{1}{6}CCl_4$, M = 280.0. Trigonal space group $R\bar{3}$ (or $R3$), referred to a hexagonal unit cell with a = 26.936(6), c = 10.796(1) Å, Z = 18 host +3 molecules CCl$_4$, U = 6 783.6 Å^3, D_c = 1.23 g cm^{-3},

$F(000) = 2\,670$. Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) $= 1.90$ cm^{-1}. The crystal used was an extended hexagon of dimensions *ca.* $0.95 \times 0.57 \times 0.57$ mm.

Crystallographic Measurements for (II).—Least-squares best-cell dimensions were obtained by a treatment of the θ, χ, ϕ setting angles of twenty-two reflections measured on a Hilger and Watts automatic diffractometer. The intensities were measured by the θ—2θ step-scan procedure with Zr-filtered Mo-K_α radiation. Background counts were taken at each end of the scan range. The changes in the intensities of three reflections monitored during data collection every 40 intensity measurements were $<6\%$, and the results were used to place the reflections on a common scale. Reflections were surveyed out to $\theta \leqslant 30°$, with an option whereby those intensities with $I \lesssim 2\sigma(I)$ were not measured. The intensity values were corrected for Lorentz-polarisation effects, but not for absorption, and 2 162 independent reflections, with $I > 2\sigma(I)$, were obtained.

Structure Analysis for (II).—The structure was solved in the centrosymmetric space group $R\bar{3}$ (this choice was justified by the success of the analysis), by direct phase-determining methods using MULTAN [7] and the 180 reflections having the largest $|E|$ magnitudes. An E map computed with that set of phases which gave the highest figure-of-merit and the lowest residual revealed all 19 of the host non-hydrogen atom positions. These approximate atomic parameters were adjusted by several cycles of full-matrix least-squares calculations using the programme CRYLSQ from the ' X-Ray '72 ' system,[8] and for anisotropic temperature factors the R value was 14.0%.

TABLE 1

(*a*) Atom co-ordinates ($\times 10^4$) of host molecule (II)

	x	y	z
O(1)	9 172(1)	7 439(1)	11 204(3)
C(2)	8 916(2)	7 777(2)	10 809(3)
C(3)	8 348(1)	7 397(2)	10 212(3)
C(4)	8 411(1)	7 119(1)	9 027(3)
C(5)	8 794(2)	6 441(2)	8 595(3)
C(6)	9 124(2)	6 197(2)	8 887(4)
C(7)	9 461(2)	6 373(2)	9 937(4)
C(8)	9 464(1)	6 782(2)	10 692(4)
C(9)	9 135(1)	7 033(1)	10 387(3)
C(10)	8 791(1)	6 862(1)	9 336(3)
C(11)	8 666(1)	7 563(1)	7 989(3)
C(12)	9 204(1)	7 743(1)	7 466(3)
C(13)	9 433(1)	8 161(2)	6 545(3)
C(14)	9 129(1)	8 416(1)	6 137(3)
C(15)	8 595(2)	8 248(2)	6 630(3)
C(16)	8 371(1)	7 834(2)	7 539(3)
C(17)	7 803(1)	6 634(2)	8 656(4)
C(18)	8 863(3)	8 064(2)	11 981(5)
O(20)	9 358(1)	8 837(1)	5 239(2)

(*b*) Atom co-ordinates, isotropic temperature factors (U) and population parameters (P.P.) for guest atoms in the clathrate of (II)

	x	y	z	U	P.P.
(i) Molecule (I)					
C(111)	1.0000	1.0000	0.090 0(30)	0.160(23)	0.50
Cl(4)	1.0000	1.0000	0.247 0(10)	0.240(8)	0.25
Cl(1)	0.930 0(10)	0.970 0(10)	0.059 0(10)	0.190(5)	0.25
(ii) Molecule (II)					
C(111)	1.0000	1.0000	0.090 0(30)	0.160(23)	0.50
Cl(42)	1.0000	1.0000	−0.065 0(10)	0.220(14)	0.25
Cl(12)	0.930 0(10)	0.970 0(10)	0.121 0(10)	0.170(4)	0.25

TABLE 2

Interatomic distances (Å) and valency angles (°) for (II), with standard deviations in parenthesis

(*a*) Bond lengths

O(1)–C(2)	1.454(5)	C(6)–C(7)	1.376(6)
O(1)–C(9)	1.368(5)	C(7)–C(8)	1.363(6)
C(2)–C(3)	1.496(6)	C(8)–C(9)	1.398(5)
C(2)–C(18)	1.525(7)	C(9)–C(10)	1.390(5)
C(3)–C(4)	1.532(5)	C(11)–C(12)	1.394(5)
C(4)–C(10)	1.528(5)	C(11)–C(16)	1.409(5)
C(4)–C(11)	1.530(5)	C(12)–C(13)	1.395(5)
C(4)–C(17)	1.552(5)	C(13)–C(14)	1.378(5)
C(5)–C(6)	1.385(6)	C(14)–C(15)	1.374(5)
C(5)–C(10)	1.391(5)	C(14)–O(20)	1.385(5)
C(15)–C(16)	1.385(6)	C(111)–Cl(1)	1.67(2)
C(111)–Cl(4)	1.69(3)	C(111)–Cl(12)	1.67(2)
C(111)–Cl(42)	1.67(3)		
Means: C(sp^3)–H	1.04		
C(sp^2)–H	0.98		
O–H	0.84		

(*b*) Valency Angles

C(9)–O(1)–C(2)	116.29(30)
C(18)–C(2)–O(1)	105.50(36)
C(10)–C(9)–O(1)	124.08(32)
C(4)–C(3)–C(2)	111.68(32)
C(11)–C(4)–C(3)	110.23(29)
C(11)–C(4)–C(10)	111.77(28)
C(5)–C(10)–C(4)	121.48(32)
C(17)–C(4)–C(11)	109.82(30)
C(16)–C(11)–C(4)	120.32(30)
C(7)–C(6)–C(5)	119.40(40)
C(8)–C(7)–C(6)	120.49(39)
C(10)–C(9)–C(8)	120.67(35)
C(13)–C(12)–C(11)	122.12(33)
C(14)–C(13)–C(12)	119.74(33)
O(20)–C(14)–C(13)	119.78(33)
C(16)–C(15)–C(14)	120.34(36)
Cl(1)–C(111)–Cl(1^{I})	116.1(13)
Cl(12)–C(111)–Cl(12^{I})	116.1(13)
C(3)–C(2)–O(1)	109.82(33)
C(8)–C(9)–O(1)	115.23(34)
C(18)–C(2)–C(3)	112.60(38)
C(10)–C(4)–C(3)	107.60(29)
C(17)–C(4)–C(3)	107.24(30)
C(17)–C(4)–C(10)	110.06(29)
C(9)–C(10)–C(4)	120.92(31)
C(12)–C(11)–C(4)	123.39(30)
C(10)–C(5)–C(6)	121.71(37)
C(9)–C(10)–C(5)	117.57(33)
C(9)–C(8)–C(7)	120.14(39)
C(16)–C(11)–C(12)	116.24(32)
C(15)–C(16)–C(11)	121.68(35)
C(15)–C(14)–C(13)	119.87(34)
O(20)–C(14)–C(15)	120.35(34)
Cl(1)–C(111)–Cl(4)	101.5(11)
Cl(12)–C(111)–Cl(42)	101.5(11)
Means: C(sp^2)–C(sp^2)–H	119.6
C(sp^3)–C(sp^3)–H	110.4
O–C(sp^3)–H	107.5
C(sp^2)–O–H	117.4
H–C(sp^3)–H	107.6

Roman numeral superscripts defined in Table 4.

Subsequent difference electron-density distributions revealed the positions of the 19 hydrogen atoms of the host molecule [two positions were found for that attached to O(20)] and the position of the guest molecule (CCl_4) in terms of two independent orientations. When these atoms were included in the least-squares calculations (with isotropic temperature factors, and with the parameters of the five guest atoms being fixed) the R value converged to a final value of 6.9% (R' 10.1%). The weighting scheme employed in the last cycles of the least-squares calculations was $w = (1.783 + 0.236\,|F| + 0.001\,|F|^2)^{-1}$.

Observed and calculated structure factors, anisotropic temperature factors, hydrogen atom co-ordinates, and thermal parameters and torsion angles for both compounds (II) and (III) are listed in Supplementary Publication No. SUP 22384 (27 pp., 1 microfiche).* Scattering factors for non-hydrogen atoms were taken from ref. 9, and for hydrogen from ref. 10, with corrections for the effects of anomalous dispersion for chlorine from ref. 11. Atomic fractional co-ordinates of the host molecule are listed in Table 1(*a*), guest-atom co-ordinates, isotropic temperature factors, and occupancy factors in Table 1(*b*), and various parameters connected with the molecular geometry are listed in Tables 2—4.

TABLE 3

Displacements (Å) of atoms from planes through various sets of atoms for (II)

Plane (*A*): C(5)—(10)

C(5) 0.001, C(6) −0.001, C(7) −0.005, C(8) 0.008, C(9) −0.005, C(10) 0.001, O(1) 0.004, C(4) 0.043, C(2) −0.241, C(3) 0.520

Plane (*B*): C(11)—(16)

C(11) −0.001, C(12) 0.003, C(13) −0.005, C(14) 0.004, C(15) −0.004, C(16) 0.002, C(4) 0.050, O(20) 0.018

Plane (*C*): O(1), C(4), C(9), C(10)

O(1) 0.002, C(4) −0.002, C(9) −0.005, C(10) 0.004, C(2) 0.281, C(3) −0.465

TABLE 4

Some short intermolecular contacts (Å) in (II)

O(20) · · · O(20$^{\text{II}}$)	2.77	O(20) · · · H(20$^{\text{III}}$)	1.94
O(20) · · · H(201$^{\text{II}}$)	1.93	C(13) · · · C(18$^{\text{IV}}$)	3.56

Roman numeral superscripts refer to the following transformations of the atom co-ordinates:

I $2 - y, 1 + x - y, z$	II $1 + x - y, x, 1 - z$
III $y, 1 - x + y, 1 - z$	IV $1 + x - y, x, 2 - z$

Crystal Data for (III).—$C_{17}H_{18}O_2$, $M = 254.3$, non-centrosymmetric tetragonal space group $P\bar{4}2_1c$, with $a = b = 12.640(2)$, $c = 17.254(4)$ Å, $Z = 8$, $U = 2\,756.7$ Å^3, $D_c = 1.22$ g cm^{-3}, $F(000) = 1\,088$. μ(Mo-K_α) = 0.85 cm^{-1}. The crystal used had dimensions *ca.* 0.60 × 0.25 × 0.25 mm.

Crystallographic Measurements for (III).—Least-squares best-cell dimensions were obtained as for compound (II). Intensities were measured as before, the intensities of two reflections being monitored after every 50 measurements; changes during data collection were <5%. 846 Independent reflections were considered observed having $I > 2\sigma(I)$.

TABLE 5

Atom co-ordinates (× 10^4) for compound (III)

	x	*y*	*z*
O(1)	5 913(3)	7 396(4)	1 130(2)
C(2)	4 787(5)	7 426(6)	1 334(3)
C(3)	4 721(5)	7 569(6)	2 216(4)
C(4)	5 244(5)	6 654(5)	2 663(3)
C(5)	6 968(6)	5 619·5)	2 634(4)
C(6)	7 901(7)	5 311(6)	2 267(5)
C(7)	8 156(6)	5 708(6)	1 546(5)
C(8)	7 481(6)	6 392(6)	1 184(4)
C(9›	6 538(5)	6 687(5)	1 541(3)
C(10)	6 282(5)	6 320(5)	2 274(3)
C(11)	5 404(5)	6 999(5)	3 514(3)
C(12)	6 210(5)	7 687(6)	3 723(4)
C(13)	6 331(6)	8 043(6)	4 482(3)
C(14)	5 630(5)	7 691(5)	5 044(3)
C(15)	4 815(5)	7 002(6)	4 849(3)
C(16)	4 707(5)	6 643(5)	4 083(3)
C(17)	4 350(6)	8 394(6)	0 929(4)
C(18)	4 277(6)	6 411(6)	1 057(4)
O(19)	5 719(4)	7 978(4)	5 807(2)

Structure Analysis for (III).—The structure was solved as for (II), from the 150 reflections having the largest $|E|$ magnitudes. An E map computed as before revealed all 19 of the non-hydrogen atom positions. These approximate atomic parameters were adjusted by several cycles of full-matrix least-squares calculations,[8] and for anisotropic temperature factors the R value was 8.9%.

A subsequent difference electron-density distribution revealed the positions of the 18 hydrogen atoms, and when these atoms were included in the least-squares calculations (with isotropic temperature factors, all hydrogen parameters being fixed) R converged to a final value of 5.2% (R' 6.1%). The weighting scheme employed in the last cycles of the

TABLE 6

Interatomic distances (Å) and valency angles (°) for (III), with standard deviations in parentheses

(*a*) Bond lengths

O(1)–C(2)	1.466(8)	C(6)–C(7)	1.378(11)
O(1)–C(9)	1.390(8)	C(7)–C(8)	1.366(11)
C(2)–C(3)	1.534(8)	C(8)–C(9)	1.392(9)
C(2)–C(17)	1.514(10)	C(9)–C(10)	1.386(8)
C(2)–C(18)	1.514(10)	C(11)–C(12)	1.386(9)
C(3)–C(4)	1.540(9)	C(11)–C(16)	1.395(9)
C(4)–C(10)	1.534(9)	C(12)–C(13)	1.394(9)
C(4)–C(11)	1.545(8)	C(13)–C(14)	1.386(9)
C(5)–C(6)	1.395(11)	C(14)–C(15)	1.390(9)
C(5)–C(10)	1.386(9)	C(14)–O(19)	1.372(7)
C(15)–C(16)	1.404(9)		

Means:	C(sp^3)–H	1.02
	C(sp^2)–H	1.04
	O–H	1.05

(*b*) Valency angles

C(9)–O(1)–C(2)	116.47(47)	C(3)–C(2)–O(1)	107.10(48)
C(17)–C(2)–O(1)	105.27(54)	C(18)–C(2)–O(1)	108.40(55)
C(8)–C(9)–O(1)	115.71(52)	C(10)–C(9)–O(1)	123.27(55)
C(17)–C(2)–C(3)	110.03(59)	C(18)–C(2)–C(3)	113.00(57)
C(4)–C(3)–C(2)	112.64(55)	C(18)–C(2)–C(17)	112.57(56)
C(10)–C(4)–C(3)	110.73(47)	C(11)–C(4)–C(3)	108.70(50)
C(11)–C(4)–C(10)	112.43(50)	C(5)–C(10)–C(4)	120.97(53)
C(9)–C(10)–C(4)	120.52(54)	C(12)–C(11)–C(4)	121.36(54)
C(16)–C(11)–C(4)	119.62(56)	C(10)–C(5)–C(6)	120.25(63)
C(7)–C(6)–C(5)	120.36(71)	C(9)–C(10)–C(5)	118.47(59)
C(8)–C(7)–C(6)	119.82(71)	C(9)–C(8)–C(7)	120.09(63)
C(10)–C(9)–C(8)	120.96(59)	C(16)–C(11)–C(12)	118.98(55)
C(13)–C(12)–C(11)	121.76(58)	C(15)–C(16)–C(11)	119.78(60)
C(14)–C(13)–C(12)	118.93(61)	C(15)–C(14)–C(13)	120.41(54)
O(19)–C(14)–C(13)	122.25(55)	O(19)–C(14)–C(15)	117.32(52)
C(16)–C(15)–C(14)	120.12(58)		

Means:	C(sp^2)–C(sp^2)–H	118.6
	C(sp^3)–C(sp^3)–H	109.6
	H–C(sp^3)–H	107.8
	C(sp^2)–C(sp^3)–H	109.0
	C(sp^2)–O–H	108.8

TABLE 7

Displacements (Å) of atoms from planes through various sets of atoms for (III)

Plane (*A*): C(5)—(10)

C(5) 0.001, C(6) −0.009, C(7) 0.006, C(8) 0.004, C(9) −0.013, C(10) 0.010, O(1) 0.005, C(4) −0.002, C(2) 0.491, C(3) 0.249

Plane (*B*): C(11)—(16)

C(11) 0.005, C(12) −0.001, C(13) 0.000, C(14) −0.002, C(15) 0.005, C(16) −0.007, C(4) 0.074, O(19) −0.045

Plane (*C*): O(1), C(4), C(9), C(10)

O(1) 0.005, C(4) −0.004, C(9) −0.011, C(10) 0.010, C(2) −0.494, C(3) 0.248, C(11) 1.049

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1978, Index issue.

least-squares calculations was $w = (2.726 - 0.139\ |F| + 0.003\ |F|^2)^{-1}$.

All calculations were carried out an an IBM 370/168 computer at Newcastle. Atomic fractional co-ordinates are listed in Table 5, and various parameters connected with the molecular geometry are listed in Tables 6 and 7.

DISCUSSION

Figure 1 shows a general view of the host molecule in the carbon tetrachloride clathrate of (II). The heterocyclic ring has a distorted half-chair conformation.

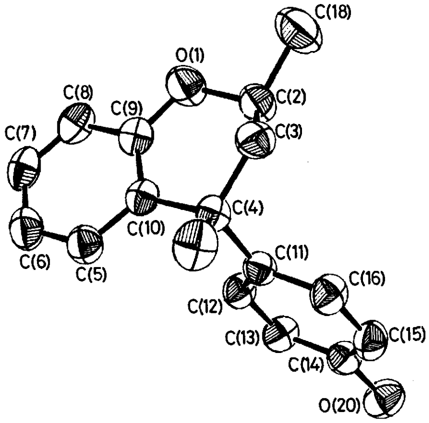

FIGURE 1 An ORTEP drawing showing a general view of 4-*p*-hydroxyphenyl-*cis*-2,4-dimethylchroman (II) in the CCl_4 clathrate; hydrogen atoms are omitted for clarity

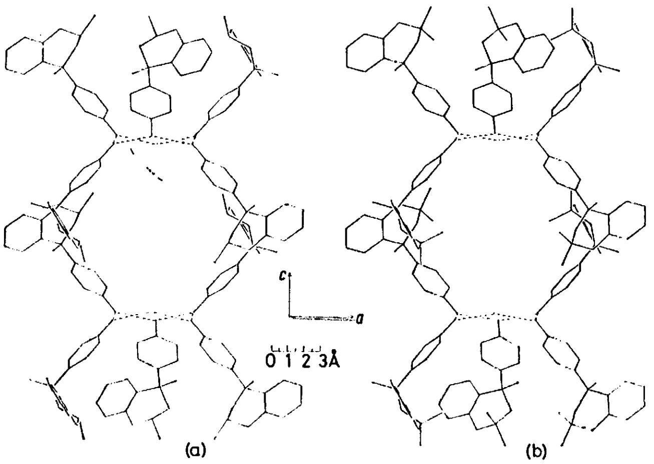

FIGURE 2 Comparative views normal to the *ac* plane for: (a) the CCl_4 clathrate of (II), and (b) the $CHCl_3$ clathrate of Dianin's compound (I), replotted from data of ref. 2*a*. In each case the two host molecules which lie above and below the cavity as viewed in this direction have been excluded, apart from their hydroxy-oxygen atoms. The disordered guest molecules are not shown

Figure 2a illustrates the host structure of (II) which is closely related to that of Dianin's compound (I) shown in Figure 2(b). A comparison of crystal data for compounds (I) and (II) is given in Table 8. In each structure groups of six molecules are linked by a network of hydrogen bonds involving their hydroxy-groups such that the oxygen atoms form a distorted hexagon, alternate molecules lying on opposite sides of its plane. Two such groups of six molecules are stacked along the *c*-axis such that their bulkier parts interlock forming a cage. The O · · · O hexamer dimension in (II) is 2.767(3) Å, compared with 2.877(3) Å for the $CHCl_3$ clathrate of (I),[2a] and the respective displacements of the oxygen atoms from their mean planes are ±0.26 and ±0.21 Å. In the case of (II) two independent hydroxy-hydrogen positions have been found with occupancies of 0.7 and 0.3; corresponding O · · · H distances and O–H · · · O angles are 1.94(7) and 1.93(7) Å, and 165(7) and 171(7)°. Allowance has been made for the disordered carbon tetrachloride guest molecule in terms of two independent orientations [Table 1(*b*)].

TABLE 8

A comparison of crystal data for compounds (I) and (II)

Host	Guest (host : guest ratio)	Space group	Lattice parameters [a]
(I) [b]	$CHCl_3$ (6 : 1)	$R\bar{3}$	*a* = 27.116 (3), *c* = 11.023 (2) Å; *Z* = 18 (host)
(II) [c]	CCl_4 (6 : 1)	$R\bar{3}$	*a* = 26.936 (6), *c* = 10.796 (1) Å; *Z* = 18 (host)

[a] Referred to a hexagonal unit cell. [b] From ref. 2*a*. [c] Present work.

The marked change in cavity shape, brought about by removal of the six inward-pointing methyl groups of (I), can be appreciated from the van der Waals surfaces shown in Figure 3. The new contour for (II) (Figure 3(b), corresponds very closely to that predicted by the theoretical removal of the appropriate ' waist ' methyl groups of (I). (The formal replacement of methyl by hydrogen is denoted by the curved broken lines in Figure 3a).

In contrast to the 2-nor-analogue already discussed, no inclusion behaviour has been found for the 4-nor-compound (III). A general view of (III) in the crystal is shown in Figure 4, the oxygen-containing ring again having a distorted half-chair conformation (see later). Figure 5 illustrates the molecular packing arrangement

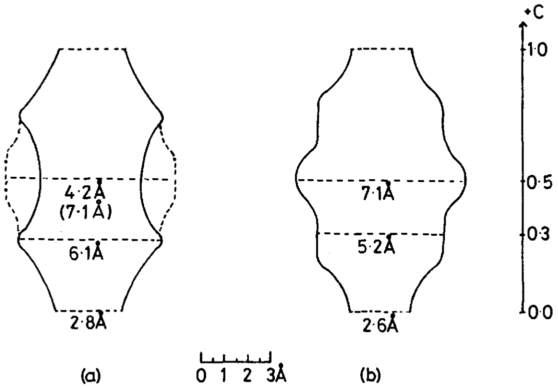

FIGURE 3 Section through the van der Waals surface of the cavity for: (a) Dianin's compound (1) as chloroform clathrate, replotted from data of ref. 2*a* (curved broken lines represent the effect of the formal removal of the ' waist ' methyl groups, see text), and (b) compound (II) as CCl_4 clathrate

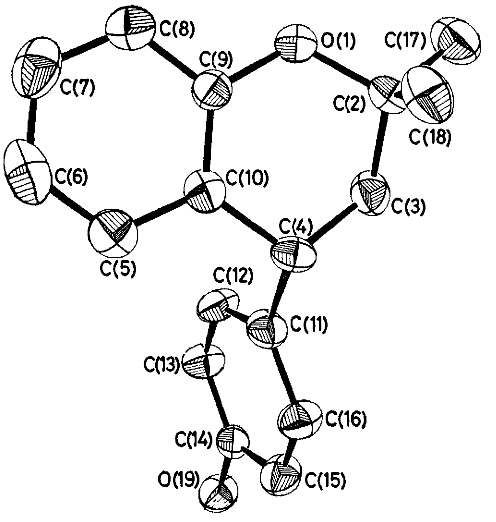

FIGURE 4 An ORTEP drawing showing a general view of the molecular structure of 4-*p*-hydroxyphenyl-2,2-dimethylchroman (III) in the crystal; hydrogen atoms are omitted for clarity

as viewed down the *c*-axis. In place of discrete hydrogen-bonded hexameric units, the present structure has infinite chains of glide-related molecules linked head-to-tail by (ether) O · · · HO hydrogen bonds. These are characterised by O · · · O and O · · · H distances of 2.82 and 1.82 Å, and the O · · · H–O angle of 156°.

Figure 6a—c shows comparative views for compounds (II), (I), and (III) respectively, looking at right-angles to the plane defined by the atoms O(1), C(9), C(10), and C(4). These views, which illustrate the changes in the conformation of the heterocyclic ring, are from the side of the molecule remote from the fused aromatic ring. The half-chair conformation of (II) is more distorted than that of (I), and the displacements of atoms C(2) and C(3) from the mean plane O(1), C(9), C(10), and C(4) are given in Table 9. Interestingly, the distorted half-chair of (III) has the opposite conformational sense from that of (I) and (II): in (III) atoms C(11) and C(3) both lie on the same side of the reference plane specified.

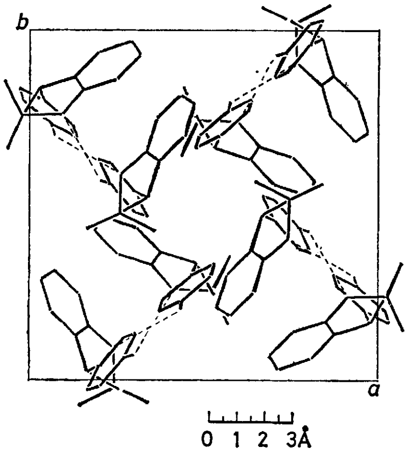

FIGURE 5 A view normal to the *ab* plane showing the molecular packing of (III) in the crystal. Intermolecular hydrogen bonds are denoted by broken lines

TABLE 9

Some selected atom displacements (Å) from the mean plane of O(1), C(9), C(10), C(4) for compounds (I), (II), and (III)

	C(2)	C(3)	C(11)	C(18)
(I)	−0.32	0.36	−1.36	0.29
(II)	−0.28	0.46	−1.38	0.15
(III)	0.49	−0.25	−1.05	2.00

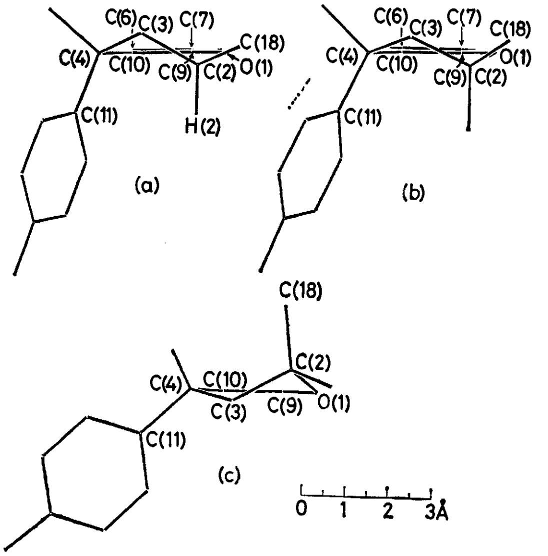

FIGURE 6 Comparative views, showing the molecular conformation, for: (a) (II), (b) (I), and (c) (III). In (a) and (b) the positions of atoms C(6) and C(7) are indicated by arrows

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