C17—C28	1.521 (7)	O2···O1'^{i}	2.73 (1)
C20—C29	1.521 (8)	O1'···O2^{ii}	2.73 (1)
C20—C30	1.532 (7)	O2'···O1^{ii}	2.65 (1)
O1'—C1'	1.297 (6)		
C1—C2—C23	109.1 (3)	C18—C17—C28	109.8 (4)
C1—C2—C24	114.4 (3)	C22—C17—C28	104.4 (3)
C3—C2—C23	107.4 (3)	C19—C20—C29	111.4 (4)
C3—C2—C24	111.4 (3)	C19—C20—C30	108.8 (4)
C23—C2—C24	108.0 (3)	C21—C20—C29	110.8 (4)
C2—C3—O4'	106.8 (2)	C21—C20—C30	109.3 (4)
C4—C3—O4'	109.5 (3)	C29—C20—C30	108.4 (4)
C1—C6—C25	113.0 (3)	O1—C28—O2	122.3 (4)
C5—C6—C7	107.2 (3)	O1—C28—C17	114.3 (4)
C5—C6—C25	108.3 (3)	O2—C28—C17	123.3 (3)
C7—C6—C25	113.7 (3)	C3—O4'—C4'	117.6 (3)
C7—C8—C26	111.3 (3)	O1'—C1'—O2'	123.4 (5)
C9—C8—C26	108.4 (3)	O1'—C1'—C2'	115.2 (5)
C14—C8—C26	109.0 (3)	O2'—C1'—C2'	121.3 (5)
C8—C14—C27	112.4 (3)	C1'—C2'—C3'	112.0 (4)
C13—C14—C27	107.7 (3)	C2'—C3'—C4'	115.8 (3)
C15—C14—C27	106.2 (3)	O3'—C4'—O4'	124.5 (4)
C16—C17—C28	110.7 (3)	O3'—C4'—C3'	124.6 (4)

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

All H atoms were placed in calculated positions on their corresponding O (O—H 0.85 Å) and C atoms (C—H 1.00 Å). These H atoms were not refined. The U_{iso} value of each H atom was assigned to be equal to the U_{eq} value of the parent atom plus 0.01. Selected geometric parameters for those atoms that are not part of the oleanolic acid five-ring framework are listed. The omitted bond lengths have e.s.d.'s of 0.005 Å and the omitted bond angles have e.s.d.'s of 0.3°. The ω-scan width was $(0.90 + 0.35\tan\theta)°$, with a θ-scan rate of 0.75–2.75° min^{-1}. The scan angle was extended by 25% on each side of each peak for background measurement. Refinement was by full-matrix least-squares methods.

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 Manual*. Data reduction: *NRCVAX DAT-RD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEPII* (Johnson, 1976) in *NRCVAX* . Software used to prepare material for publication: *NRCVAX TABLES* (Version of January 1994).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1288). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
Dai, Y., Hang, B. Q., Li, P. Z. & Tan, L. W. (1989). *Acta Pharm. Sinica*, **10**, 381–384.
Enraf–Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Jia, B. Z. (1996). Personal communication.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Ohigashi, H., Takamura, H., Koshimizu, K., Tokuda, H. & Ito, Y. (1986). *Cancer Lett.* **30**, 143–151.
Schalkwyk, T. G. D. van & Kruger, G. J. (1974). *Acta Cryst.* B30, 2261–2264.
Singh, G. B., Singh, S., Bani, S., Gupta, B. D. & Banerjee, S. K. (1991). *J. Pharm. Pharmacol.* **44**, 456–458.

Inclusion Complex of (S)-1,3-Butanediol with (S,S)-(+)-*trans*-2,3-Bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane

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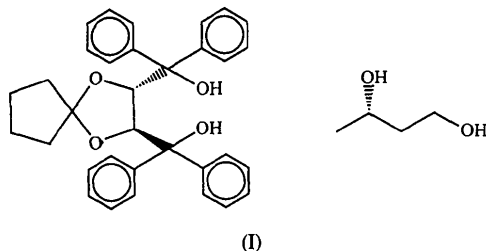
Abstract

(S)-1,3-Butanediol (guest), $C_4H_{10}O_2$, was found to be resolved from the racemate by inclusion crystallization with (S,S)-(+)-*trans*-2,3-bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane (host), $C_{33}H_{32}O_4$. The unit cell of the crystal contains two pairs of host and guest molecules. There are four crystallographically independent hydrogen bonds, which form a belt-like structure along the *b* axis of the unit cell. The inclusion complex appears to be stabilized by hydrogen bonds and van der Waals interactions.

Comment

An optically active host having a 4,5-bis(hydroxydiphenylmethyl)-1,3-dioxolane framework is one of the most useful hosts, because it is derived simply from optically active tartaric acid (Seebach, Beck, Imwinkelried, Roggo & Wonnacott, 1987) and furthermore, it is capable of efficiently resolving many racemates (Toda & Tanaka, 1988). A prediction of optimum host–guest pairs, however, is very difficult since the optical resolution capability is often changed dramatically by a slight difference in the chemical structure in a host (Toda, Sato, Nassimbeni & Niven, 1991; Toda, Tanaka, Leung, Meetsma & Feringa, 1994; Toda, Matsuda & Tanaka, 1991). To enable the prediction of optimal host–guest

pairs, we have studied the atomic interactions in an inclusion complex, (I), involving both host and guest molecules, by a single-crystal X-ray structural analysis.

for optical resolution. We intend to investigate a series of similar inclusion systems in order to resolve this problem.
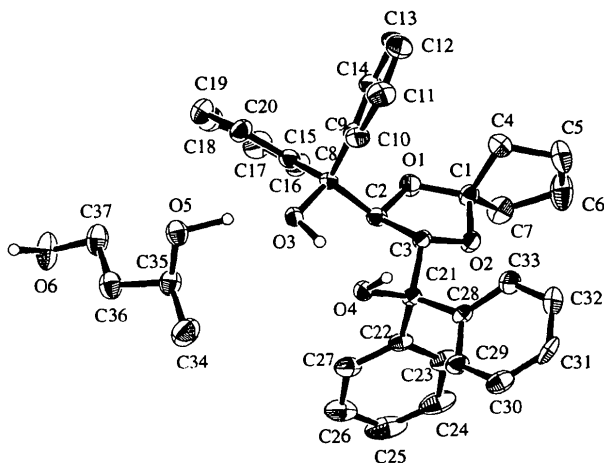
(I)

Fig. 1. The labeling scheme and displacement ellipsoids (30% probability) for the title inclusion complex.

The labeling scheme and displacement ellipsoids for the inclusion complex are depicted in Fig. 1. The C5—C6 bond is shorter than any other C—C bonds in the cyclopentyl group, which might be attributed to disorder of the C5 and C6 atoms. A similar example is reported in (E)-stilbene (Ogawa, Sato, Yoshimura, Takeuchi & Toriumi, 1992). Other bond distances and all bond angles in this inclusion complex are within the ranges found for other inclusion complexes (Toda, Sato, Nassimbeni & Niven, 1991; Toda et al., 1993). The displacement parameters of the outermost atoms of the host and guest molecules are relatively large. The asymmetric unit contains one host and one guest molecule (Fig. 2) connected by hydrogen bonds. The guest molecule lies around the crystallographic screw axis, forming 'head-to-tail' hydrogen bonds with the hydroxyl groups of both ends. This guest–guest hydrogen bond repeats along the b axis like a belt. A host molecule makes two hydrogen bonds to two guest molecules from the other side of the guest–guest pair, like a 'frill' on the belt. The outermost edge of this 'frill' consists of the hydrophobic groups of the host molecules. In addition to the hydrogen bonds, these van der Waals interactions also play an important role in stabilizing the crystal structure. There are four types of hydrogen bonds: (a) an intramolecular hydrogen bond in the host [O3···O4 2.663(3) Å]; (b) an intermolecular hydrogen bond between an OH group in the host and the 1-OH group in the guest [O4···O6^i 2.672(4) Å]; (c) an intermolecular hydrogen bond between an OH group in the host and the 3-OH group in the guest [O3···O5 2.842(4) Å]; (d) an intermolecular hydrogen bond between the 1-OH group in the guest and the 3-OH group in another guest [O5···O6^{ii} 2.701(4) Å] [symmetry codes: (i) x, $1+y$, z; (ii) $1-x$, $\frac{1}{2}+y$, $1-z$]. The relative strengths of the hydrogen bonds based on O···O distances is $(a) > (b) > (d) > (c)$, which implies that intramolecular hydrogen bonds primarily determine the conformation of the host molecules. These results lead to the conclusion that hydrogen bonds and van der Waals contacts play an important role in inclusion crystallization. It is difficult, however, to conclude that hydrogen bonding alone is responsible
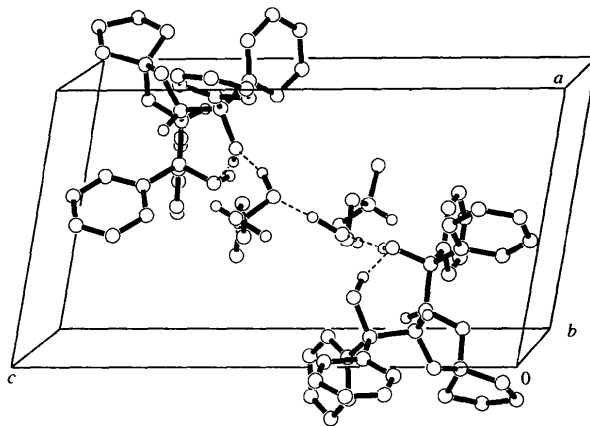

Fig. 2. A perspective view of the title structure showing the hydrogen bonds as dashed lines.

Experimental

A suitable single crystal of (I) was selected from those resolved from the racemate in diethyl ether.

Crystal data

C₃₃H₃₂O₄.C₄H₁₀O₂	Cu $K\alpha$ radiation
$M_r = 582.74$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 16
$P2_1$	reflections
$a = 9.447(1)$ Å	$\theta = 27.6–28.4°$
$b = 10.037(2)$ Å	$\mu = 0.653$ mm^{-1}
$c = 17.040(2)$ Å	$T = 296.2$ K
$\beta = 100.21(1)°$	Prismatic
$V = 1590.1(4)$ Å^3	$0.30 \times 0.30 \times 0.05$ mm
$Z = 2$	Colorless
$D_x = 1.217$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-5R diffractometer	$R_{int} = 0.0413$
ω–2θ scans	$\theta_{max} = 60°$
Absorption correction: none	$h = -10 \rightarrow 0$
2696 measured reflections	$k = -11 \rightarrow 0$
2526 independent reflections	$l = -18 \rightarrow 19$
2086 reflections with	3 standard reflections
$I > 3\sigma(I)$	every 150 reflections
	intensity decay: 0.92%

Refinement

Refinement on F	$\Delta\rho_{max} = 0.17$ e Å^{-3}
$R = 0.0432$	$\Delta\rho_{min} = -0.18$ e Å^{-3}
$wR = 0.0553$	Extinction correction:
$S = 1.260$	Zachariasen (1967) type
2086 reflections	2, Gaussian isotropic
388 parameters	Extinction coefficient:
H atoms not refined	0.08 (1)
$w = 1/[\sigma^2(F_o)$	Scattering factors from
$+ 0.00090|F_o|^2]$	*International Tables for*
$(\Delta/\sigma)_{max} = 0.0010$	*Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.432 (5)	C1—C7	1.505 (6)
O1—C2	1.426 (5)	C2—C3	1.543 (6)
O2—C1	1.423 (4)	C2—C8	1.556 (5)
O2—C3	1.414 (4)	C3—C21	1.545 (5)
O3—C8	1.431 (4)	C4—C5	1.515 (7)
O4—C21	1.424 (4)	C5—C6	1.471 (8)
C1—C4	1.509 (6)	C6—C7	1.544 (8)
C1—O1—C2	110.2 (3)	C3—C2—C8	118.1 (3)
C1—O2—C3	107.3 (3)	O2—C3—C2	102.1 (3)
O1—C1—O2	104.7 (3)	O2—C3—C21	109.5 (3)
O1—C1—C4	112.9 (3)	C2—C3—C21	118.4 (3)
O1—C1—C7	114.0 (4)	C1—C4—C5	104.1 (4)
O2—C1—C4	111.5 (3)	C4—C5—C6	106.3 (4)
O2—C1—C7	108.2 (3)	C5—C6—C7	108.5 (4)
C4—C1—C7	105.6 (3)	C1—C7—C6	103.6 (4)
O1—C2—C3	103.0 (3)	O3—C8—C2	107.2 (3)
O1—C2—C8	110.1 (3)	O4—C21—C3	106.6 (3)

Table 2. *Contact distances (Å)*

O3···O5	2.842 (4)	O5···O6^{ii}	2.701 (4)
O4···O6^{i}	2.672 (4)		

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

Data collection and cell refinement was carried out using *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). The scan rate was 16° min^{-1} (in ω) and the scan width was $(1.63 + 0.30\tan\theta)°$. The ratio of peak counting time to background counting time was 2:1. Data reduction was performed using *TEXSAN* (Molecular Structure Corporation, 1993). The structure was solved with *SHELXS86* (Sheldrick, 1985) and refined using *TEXSAN*. Refinement was by full-matrix least-squares methods, with anisotropic displacement parameters for all non-H atoms. Hydroxyl H atoms were located in difference Fourier maps and all other H atoms were placed in calculated positions. *TEXSAN* software was also used to prepare the material for publication.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Ogawa, K., Sano, T., Yoshimura, S., Takeuchi, Y. & Toriumi, K. (1992). *J. Am. Chem. Soc.* **114**, 1041–1051.

Seebach, D., Beck, A. K., Imwinkelried, R., Roggo, S. & Wonnacott, A. (1987). *Helv. Chim. Acta*, **70**, 954–974.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Toda, F., Matsuda, S. & Tanaka, K. (1991). *Tetrahedron Asymm.* **2**, 983–986.

Toda, F., Sato, A., Nassimbeni, L. R. & Niven, M. L. (1991). *J. Chem. Soc. Perkin Trans. 2*, pp. 1971–1975.

Toda, F. & Tanaka, K. (1988). *Tetrahedron Lett.* **29**, 551–554.

Toda, F., Tanaka, K., Leung, C. W., Meetsma, A. & Feringa, B. L. (1994). *J. Chem. Soc. Chem. Commun.* pp. 2371–2372.

Toda, F., Tanaka, K., Ootani, M., Hayashi, A., Miyahara, I. & Hirotsu, K. (1993). *J. Chem. Soc. Chem. Commun.* pp. 1413–1415.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

A 2H-Pyrano[3,2-a]indolizine Derivative

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Abstract

The indolizine and pyrano[3,2-a]indolizine skeletons of 10-ethyl-2-oxo-2H-pyrano[3,2-a]indolizine-3-carbonitrile, $C_{14}H_{10}N_2O_2$, are planar [mean deviations 0.003 (2) and 0.019 (2) Å, respectively]. The planar pyrone ring [mean deviation 0.009 (2) Å], fused at the 1- and 2-positions of the indolizine ring, is also almost coplanar with the indolizine ring [dihedral angle 2.3 (1)°]. The delocalized ring system of the indolizine skeleton extends to the fused 2-pyrone ring, resulting in a significant decrease in the bond-alternation characteristics of the 2-pyrone moiety.