satisfactory because of the high value of $R$ (0.087) and the presence in the final $\Delta\rho$ map of considerable residual electron density around the ring C atoms and the tail O atoms. A disorder model was assumed, involving the two alternative half-chair ring conformations and the carboxylic acid group flipping over two symmetrical positions obtained by reflection through the plane of the chain, with site-occupancy factors of 0.5 for all double-positioned atoms. The final accepted solution of the phase problem, with the highest symmetry and the highest figure of merit, *i.e.* in the orthorhombic *Cmca* space group, appeared to be consistent with the proposed disordered structure and was accepted as the correct one. The H atoms of the methyl groups were placed in calculated positions using the $\Delta\rho$ map as a guide. During the following refinement, the methyl groups were treated as rigid bodies with free rotation around the methyl C—C bonds (*SHELXL*93; Sheldrick, 1993). The H atoms bonded to the C2, C3 and C4 atoms were added at calculated positions and refined using a riding model. The carboxyl hydrogen was placed in a calculated position to form the best hydrogen bond and then freely refined. To further verify the validity of the structural model adopted, the coordinates and anisotropic displacement parameters, refined in the orthorhombic lattice, were transformed again to the monoclinic system and refined. As expected, no significant change was found and the residual error index $R$ converged to 0.0495 for 330 parameters refined with 1989 unique reflections. Only the results of the refinement in orthorhombic space group *Cmca* are reported and deposited.

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1267). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1997). C**53**, 511–513

# Absolute Structure of (Thian-5-one 1,1-dioxide)-3-spiro-3′-(5′-*O*-*tert*-butyldimethylsilyl-3′-deoxy-1′,2′-*O*-isopropylidene-α-D-*xylo*-pentofuranose), a Novel Type of Spirosugar

GÉRALD BERNARDINELLI,[a] JEAN M. J. TRONCHET[b] AND IMRE KOVACS[b]

[a]*Laboratoire de Cristallographie, Université de Genève, 24 Quai E. Ansermet, CH-1211 Genève 4, Switzerland, and* [b]*Département de Chimie Pharmaceutique, Université de Genève, CH-1212 Genève 4, Switzerland. E-mail: gerald.bernardinelli@cryst.unige.ch*

*(Received 17 June 1996; accepted 21 November 1996)*

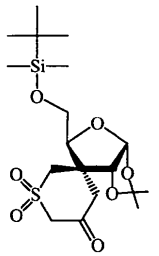

## Abstract

The absolute structure of the title compound, $C_{18}H_{32}O_7SSi$, has been determined. The thianone ring adopts a chair conformation whereas the furanose ring exists in an envelope conformation. No short interatomic distance was observed in the molecular packing.


## Comment

The discovery of the powerful anti-HIV-1 activity of the TSAO derivatives (Ingate, Camarasa, De Clercq & Balzarini, 1995) has renewed interest in spironucleosides. The title compound, (I), has been prepared (Tronchet, Kovacs & Bernardinelli, 1996) as a synthetic building block to be used for the synthesis of a novel type of spironucleoside. The two electron-withdrawing groups of the thianone *S,S*-dioxide ring afford a large flexibility for the further functionalization of the ring in such a way as to design hopefully, biologically active derivatives. The stereospecific spiro insertion of the thianone ring has been carried out *via* the nucleophilic attack of the conjugate base of dimethylsulfone upon the *Z* diasteroisomer of the corresponding 3-deoxy-3-methoxycarbonylmethylidenefuranose derivative. An

X-ray analysis was deemed necessary to assess the geometrical features of this exotic spirosugar and to confirm its configuration established by $^1H$ NMR.



(I)

The minimum values of the asymmetry parameters (Nardelli, 1983) show that the 3-oxothiane 1,1-dioxide ring adopts a quasi-perfect chair conformation, whereas the furanose ring exists in an envelope conformation, with the C4 atom out of the plane [$\Delta C_s$(C4) = 0.030 (4)]. The dioxolane ring, *cis*-fused to the furanose ring, exhibits a twist conformation associated with a quasi-ideal $C_2$ symmetry passing through the C1 atom [$\Delta C_2$(C1) = 0.006 (3)].

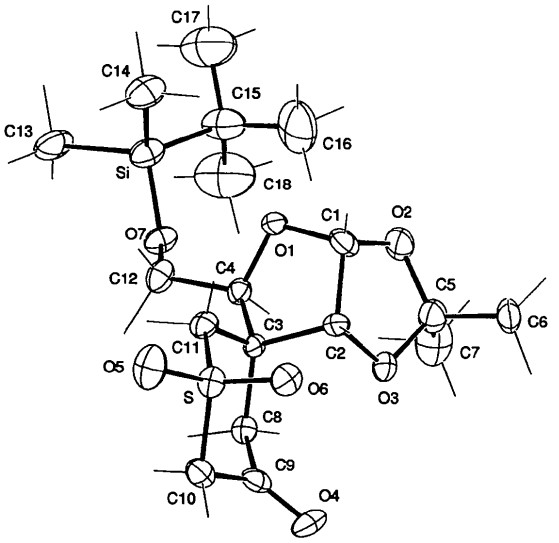



Fig. 1. View of the title compound with the atom labelling. Displacement ellipsoids are represented at the 30% probability level.

## Experimental

Crystals of (I) [m.p. 433.8–434.2 K; $[\alpha]_D^{27}$ = +104.9° ($c$ = 1.1, $CHCl_3$)] were grown at room temperature from benzene solution (Tronchet, Kovacs & Bernardinelli, 1996).

*Crystal data*

| | |
|---|---|
| $C_{18}H_{32}O_7SSi$ | Cu $K\alpha$ radiation |
| $M_r$ = 420.6 | $\lambda$ = 1.54184 Å |
| Orthorhombic | Cell parameters from 20 reflections |
| $P2_12_12_1$ | $\theta$ = 14.5–30.5° |
| $a$ = 6.6446 (5) Å | $\mu$ = 2.123 $mm^{-1}$ |
| $b$ = 9.4721 (8) Å | $T$ = 293 K |
| $c$ = 35.046 (2) Å | Needle |
| $V$ = 2205.7 (2) $Å^3$ | 0.500 × 0.130 × 0.026 mm |
| $Z$ = 4 | Colourless |
| $D_x$ = 1.266 Mg $m^{-3}$ | |
| $D_m$ not measured | |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | 2501 reflections with $F > 4\sigma(F)$ |
| $\omega$–$2\theta$ scans | $R_{int}$ = 0.031 |
| Absorption correction: analytical by integration (Blanc, Schwarzenbach & Flack, 1991) | $\theta_{max}$ = 54.96° |
| | $h = 0 \rightarrow 7$ |
| | $k = 0 \rightarrow 10$ |
| | $l = 0 \rightarrow 36$ (and all Friedel pairs) |
| $T_{min}$ = 0.78, $T_{max}$ = 0.95 | 2 standard reflections |
| 3412 measured reflections | every 100 reflections |
| 2746 independent reflections | intensity decay: 6.5% |

*Refinement*

| | |
|---|---|
| Refinement on $F$ | $\Delta\rho_{max}$ = 0.738 e $Å^{-3}$ |
| $R$ = 0.059 | $\Delta\rho_{min}$ = −0.314 e $Å^{-3}$ |
| $wR$ = 0.041 | Extinction correction: none |
| $S$ = 3.101 | Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV) |
| 2501 reflections | |
| 278 parameters | |
| H atoms: see below | Absolute configuration: Flack (1983) |
| $w = 1/\sigma^2(F_o)$ | |
| $(\Delta/\sigma)_{max}$ = 0.000182 | Flack parameter = 0.02 (5) |

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

| | | | |
|---|---|---|---|
| S—O5 | 1.442 (7) | O3—C5 | 1.430 (11) |
| S—O6 | 1.437 (6) | O4—C9 | 1.217 (11) |
| S—C10 | 1.794 (11) | C1—C2 | 1.542 (14) |
| S—C11 | 1.771 (10) | C2—C3 | 1.551 (11) |
| O1—C1 | 1.427 (11) | C3—C4 | 1.537 (11) |
| O1—C4 | 1.416 (10) | C3—C8 | 1.547 (12) |
| O2—C1 | 1.392 (12) | C3—C11 | 1.530 (12) |
| O2—C5 | 1.418 (14) | C8—C9 | 1.501 (12) |
| O3—C2 | 1.428 (10) | C9—C10 | 1.510 (13) |
| O5—S—O6 | 118.2 (4) | C1—C2—C3 | 103.8 (7) |
| C10—S—C11 | 100.5 (5) | C2—C3—C4 | 100.2 (6) |
| C1—O1—C4 | 107.5 (7) | C8—C3—C11 | 110.4 (7) |
| C1—O2—C5 | 111.6 (8) | O1—C4—C3 | 103.7 (6) |
| C2—O3—C5 | 109.9 (7) | O2—C5—O3 | 105.8 (8) |
| O1—C1—C2 | 106.5 (7) | C3—C8—C9 | 112.5 (7) |
| O2—C1—C2 | 105.6 (8) | C8—C9—C10 | 115.3 (8) |
| O3—C2—C1 | 104.2 (7) | S—C10—C9 | 107.7 (7) |
| O3—C2—C3 | 109.1 (7) | S—C11—C3 | 116.8 (6) |
| C11—S—C10—C9 | 53.1 (7) | O1—C1—C2—C3 | −3.2 (9) |
| C10—S—C11—C3 | −51.7 (7) | O2—C1—C2—O3 | −6.0 (9) |
| C4—O1—C1—C2 | −23.9 (9) | C1—C2—C3—C4 | 26.0 (8) |
| C1—O1—C4—C3 | 41.6 (8) | C2—C3—C4—O1 | −41.0 (8) |
| C5—O2—C1—C2 | −4.7 (10) | C11—C3—C8—C9 | −54.4 (9) |
| C1—O2—C5—O3 | 13.6 (10) | C8—C3—C11—S | 53.4 (9) |
| C5—O3—C2—C1 | 14.5 (8) | C3—C8—C9—C10 | 65.1 (10) |
| C2—O3—C5—O2 | −17.6 (9) | C8—C9—C10—S | −65.4 (9) |

All non-methyl H atoms were observed and refined with fixed $U_{iso}$ values. The coordinates of all methyl H atoms were calculated.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *Xtal*3.2 *LATCON* (Hall, Flack & Stewart,

1992). Data reduction: *Xtal*3.2 *REFCAL LSABS SORTRF*. Program(s) used to solve structure: *MULTAN*87 (Main *et al.*, 1987). Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2 *ORTEP*. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: PA1244). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# A Novel Function of an Atropisomeric Flavin Model as a Host Compound


YASUSHI KAWAI, JUN KUNITOMO AND ATSUYOSHI OHNO

*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan. E-mail: kawai@scl.kyoto-u.ac.jp*


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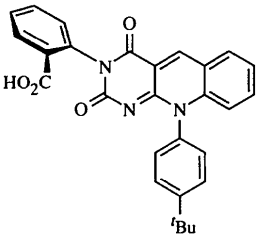
## Abstract

2-[10-(4-*tert*-Butylphenyl)-2,4(3*H*,10*H*)-dioxopyrimido[4,5-*b*]quinolin-3-yl]benzoic acid methanol solvate forms a crystalline 1:1 host–guest inclusion complex with methanol, $C_{28}H_{23}N_3O_4.CH_3OH$, through a hydrogen-bonding network.


## Comment

We have synthesized several atropisomeric flavoenzyme models in order to investigate the stereochemical reactivities of these compounds (Ohno *et al.*, 1994, 1996). In the course of our studies, we have also carried out X-ray crystallographic analyses of some of these compounds both for determination of absolute configuration (Kawai, Kunitomo & Ohno, 1997) and for structural interest in compounds with axial chirality (Ohno *et al.*, 1994; Ohno, Kunitomo & Kawai, 1997), and found that the title compound, 2-[10-(4-*tert*-butylphenyl)-3-(2-carboxyphenyl)pyrimido[4,5-*b*]quinoline-2,4(3*H*,10*H*)-dione, (I), affords a crystalline inclusion complex with methanol through hydrogen bonding.




(I)

An *ORTEP*II (Johnson, 1976) drawing and a stereoview of the 1:1 inclusion complex of (I) with methanol are given in Figs. 1 and 2, respectively. They show that hydrogen bonds exist between the hydroxyl group of the carboxyl group and the O atom of methanol (O4—H10···O5), as well as between the hydroxyl group of methanol and the carbonyl group of the flavin skeleton (O5—H27···O1). The same enantiomers of (I) are linked through this hydrogen-bonding network (Fig. 2).

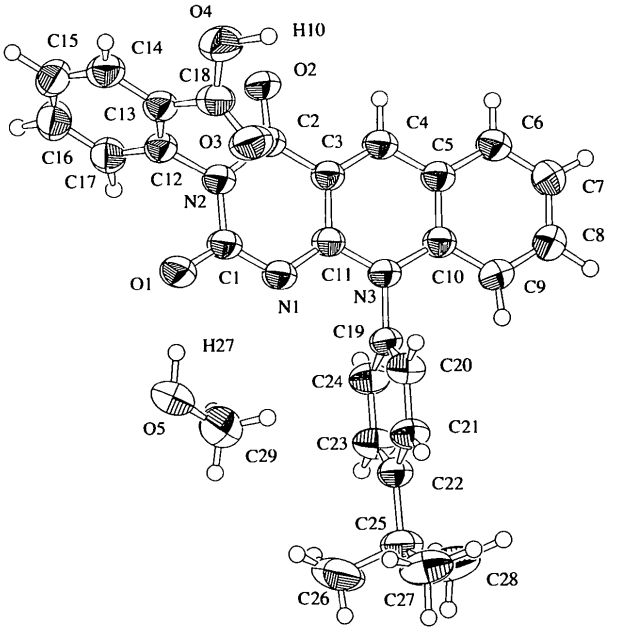



Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I).$CH_3OH$ showing displacement ellipsoids at the 50% probability level.