Acta Cryst. (1974). B**30**, 597

The Structure of Sporidesmin G Etherate*

By M. Przybylska and E. M. Gopalakrishna†

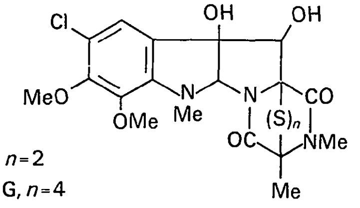
Division of Biological Sciences, National Research Council of Canada, Ottawa, K1A 0R6, Canada

(*Received* 1 *June* 1973; *accepted* 12 *October* 1973)

Sporidesmin G etherate, $C_{18}H_{20}O_6N_3S_4Cl.(C_2H_5)_2O$, a tetrathio compound, was obtained by treating sporidesmin (a disulphide) with dihydrogen disulphide. The crystals belong to the space group $P2_12_12_1$ with unit-cell dimensions: $a=15{\cdot}160$ (4), $b=21{\cdot}369$ (4) and $c=8{\cdot}978$ (4) Å; $Z=4$. The data were collected with a Picker automatic diffractometer. The structure was solved by the application of the tangent formula and refined by block-diagonal least-squares cycles to a final R value of 0·057. The tetrathiopiperazinedione moiety in sporidesmin G was found to be closely similar to the structure of an enantiomer described recently by Davis & Bernal [*Proc. Natl. Acad. Sci. U.S.* (1973). **70**, 279–283].

Introduction

The production of the toxin, sporidesmin G, by *Pithomyces chartarum* was reported by Francis, Rahman, Safe & Taylor (1972). Its structure was found to be closely related to that of sporidesmin, which was X-ray analysed by Fridrichsons & Mathieson (1965). Sporidesmin has an epidithio-piperazinedione ring, whereas sporidesmin G is a tetrasulphide as shown below. The c.d. and n.m.r. spectra of the metabolite were identical with those of a cyclic tetrasulphide, obtained from sporidesmin by the reaction with dihydrogen disulphide. This work was carried on such a semi-synthetic compound prepared by A. Taylor and S. Safe.



Sporidesmin, $n=2$
Sporidesmin G, $n=4$

The spectroscopic analysis indicated the presence of a single conformation of the epitetrathio group. Its stereochemistry, however, could not be assigned and since a number of conformers seemed possible, an X-ray analysis was suggested by Dr A. Taylor.

The results of this investigation have been published in a preliminary communication (Przybylska, Gopalakrishna, Taylor & Safe, 1973).

Experimental

Sporidesmin G etherate, $C_{18}H_{20}O_6N_3S_4Cl.(C_2H_5)_2O$, F.W. 612·23. Orthorhombic, $a=15{\cdot}160$ (4), $b=21{\cdot}369$ (4), $c=8{\cdot}978$ (4) Å. $V=2908{\cdot}5$ Å^3, $Z=4$. Space group $P2_12_12_1$. $D_m=1{\cdot}403$ g cm^{-3}, by flotation in a solution of KI; $D_c=1{\cdot}398$ g cm^{-3}. $F(000)=1280$, $\mu(\text{Cu } K\alpha)=40{\cdot}1$ cm^{-1}.

The space group was established from systematic absences from precession photographs taken with the X-ray beam parallel to the a and b axes. The acicular [001] colourless prisms, crystallized from ether, were obtained from Dr A. Taylor. The unit-cell dimensions were derived from the measurements of the high-order axial reflexions with Cu radiation ($K\alpha_1$ and $K\alpha_2$). The data were collected at room temperature with a Picker four-circle automatic diffractometer. Out of 2819 independent reflexions measured within $2\theta \leq 130°$, 2152 reflexions had significant counts. The threshold was taken as a net count of 50 or 10% of the total background count, whichever was higher. The $\theta/2\theta$ scanning method was used with Ni-filtered Cu radiation at a take-off angle of 5·3°. Background measurements for 20 s were taken at each end of the scans. High intensities were remeasured with lower current settings. The standard reflexions were determined after every 50 reflexions. The crystal developed a yellowish tinge on exposure to the X-rays, but this did not affect the intensities. Fifty reflexions estimated at the start of the data collection were remeasured at the end and no significant changes were observed. In addition, a freshly prepared batch of crystals was obtained several months later and over a hundred reflexions were checked with satisfactory results. The crystal was $0{\cdot}1 \times 0{\cdot}1 \times 0{\cdot}2$ mm and it was mounted with the axis of elongation parallel to the φ axis. Absorption corrections were not applied.

Solution of the structure and its refinement

The attempts to solve the structure from a sharpened Patterson synthesis had failed, but success was achieved with the direct phasing method (Karle & Hauptman, 1956). The scale factor and the overall isotropic temperature factor were evaluated by Wilson's method (1942). The scale factor increased by 50% during the refinement.

Since the first trials using only four reflexions with assigned phases also failed, it was decided to increase their number to the seven with E values listed below:

---

* Issued as N.R.C.C. No. 13774.

† National Research Council of Canada Postdoctorate Fellow. Present address: Department of Physics, University of Mysore, Mysore 570006, India.

h	k	l	$\|E\|$	α
4	23	0	3·18	0
0	18	7	3·05	0
1	6	0	2·69	$\pi/2$
12	7	1	2·77	$\pi/2$
15	11	0	2·73	$\pm\pi/2$
4	3	5	2·50	$\pm\pi/4$, $\pm 3\pi/4$
8	4	0	2·49	0, π

The first three were origin-defining and had their phases fixed, but the reflexion 12,7,1 was to have different phases assigned to it for the subsequent combinations; however, this was not necessary. Of the first sixteen trials, carried out with 97 E's $\geq 1·8$, with one cycle each, two were more promising. Initially they differed only in the phase assignment ($3\pi/4$ and $-3\pi/4$) for the reflexion 435. It was, therefore, possible to combine the results by assuming this phase to be π and by eliminating all the E values for which the phases differed appreciably.

74 E's were used for the next step in the tangent formula refinement, which consisted of ten cycles with five iterations each. The number of E's was increased gradually to 265 ($E \geq 1·51$). All but two of these had their phases assigned and the R(Karle) of 0·28 was reached. A program written by S. R. Hall, C. P. Huber and F. R. Brisse, modified by G. I. Birnbaum was used. The resultant E map was satisfactory; it revealed the positions of the five heavy atoms. The structure was then easily solved from ϱ_0 and $\Delta\varrho$ syntheses.

The R value had decreased from 0·19 to 0·084 after four cycles of the anisotropic least-squares refinement. The hydrogen atoms were located from two sets of difference maps calculated with reflexions of $\sin^2\theta \leq 0·8$ and separated by two cycles of least squares. Five hydrogen atoms of the ether molecule did not refine well due to the large thermal motion or disorder and their parameters were, therefore, kept fixed.

Six additional cycles completed the refinement. The final average shift for the non-hydrogen atoms was one fifth of the corresponding e.s.d. values and the maximum shifts were obtained for the C(22) atom of the ether (up to 0·9 of the e.s.d.).

The atomic scattering factors were from *International Tables for X-ray Crystallography* (1962), except for the hydrogen atoms, for which the values of Stewart, Davidson & Simpson (1965) were used. The refinement was carried out by the block-diagonal approximation of the least-squares method, minimizing the expression $\sum\omega(|F_o|-|F_c|)^2$. Total shifts were used throughout, but for the last few cycles factors of 0·7 and 0·5 were applied.

Uniform values of mean $\omega(\Delta F)^2$ over various ranges of observed structure factors and $\sin^2\theta$ were obtained with the weighting scheme:

$$\sqrt{\omega} = 1/\{1+[(|F_o|-P_2)/P_1]^4\}^{1/2}$$

where

$$P_1 = 35 \quad \text{and} \quad P_2 = 40\,.$$

In Table 1 the fractional coordinates of all the non-hydrogen atoms are presented and in Table 2 their vibrational parameters are listed. The coordinates and temperature factors of the hydrogen atoms are given in Table 3. The observed and calculated structure factors are shown in Table 4. The structure factors for the unobserved reflexions were calculated, but they were excluded from the refinement procedure. The agreement summary is given in Table 5.

Table 1. *Final fractional coordinates* ($\times 10^4$) *and their estimated standard deviations*

	x/a	y/b	z/c
Cl	9486 (1)	7074 (1)	3194 (3)
S(1)	3125 (2)	5019 (1)	1516 (4)
S(2)	3658 (2)	4342 (1)	217 (4)
S(3)	4461 (2)	4831 (1)	−1261 (3)
S(4)	5692 (2)	4640 (1)	−564 (2)
N(1)	4657 (4)	4828 (3)	3084 (7)
N(2)	5373 (3)	5697 (2)	1166 (6)
N(3)	5891 (4)	6766 (2)	884 (6)
O(1)	4130 (3)	6268 (2)	1161 (8)
O(2)	5865 (4)	4212 (2)	2774 (7)
O(3)	6967 (3)	5352 (2)	2924 (5)
O(4)	7299 (3)	5713 (2)	−809 (5)
O(5)	6402 (4)	7948 (2)	2364 (6)
O(6)	8106 (4)	8043 (2)	3379 (6)
O(7)	2135 (4)	8338 (2)	2869 (7)
C(1)	4092 (5)	5318 (4)	2570 (10)
C(2)	4533 (4)	5796 (3)	1505 (8)
C(3)	5917 (4)	6133 (3)	294 (7)
C(4)	5793 (4)	5095 (3)	1234 (7)
C(5)	5430 (5)	4672 (3)	2439 (8)
C(6)	6772 (4)	5256 (3)	1426 (7)
C(7)	6872 (4)	5868 (3)	528 (7)
C(8)	7307 (4)	6407 (3)	1340 (7)
C(9)	6712 (4)	6888 (3)	1460 (8)
C(10)	6977 (5)	7451 (3)	2194 (8)
C(11)	7832 (5)	7503 (3)	2675 (8)
C(12)	8412 (5)	6996 (3)	2531 (8)
C(13)	8149 (5)	6446 (3)	1870 (9)
C(14)	4327 (6)	4379 (5)	4222 (11)
C(15)	3692 (6)	5695 (5)	3863 (13)
C(16)	5467 (6)	7234 (3)	−79 (10)
C(17)	5716 (6)	7833 (4)	3448 (12)
C(18)	8308 (6)	8543 (3)	2376 (10)
C(19)	1064 (8)	8941 (7)	4115 (11)
C(20)	1863 (7)	8599 (4)	4282 (11)
C(21)	2836 (8)	7928 (5)	3106 (15)
C(22)	3059 (12)	7608 (8)	1894 (18)

Description and discussion of the structure

A projection of the structure of sporidesmin G is presented in Fig. 1. It was obtained with Johnson's (1965) *ORTEP* program and shows thermal ellipsoids, enclosing the 50% probability level.

The bond lengths and the valency angles are shown in Fig. 2. The e.s.d.'s cited in the legend and used throughout this report were derived from the least-squares calculations and they are probably underestimated.

The C=O bond lengths give the average of 1·220 Å and they are in good agreement with Sutton's (1965) value of 1·215 ± 0·005 Å. For the benzene-ring bonds an average of 1·386 Å was obtained and for its angles 120·0°.

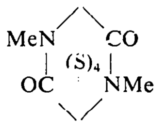
The C–H bonds range from 0·83 to 1·26 Å with e.s.d.'s from 0·05 to 0·13 Å. Their average is 1·01 Å. The average value for CCH and HCH angles is 109·9° and they range from 80·3 to 126·2°.

Fridrichsons & Mathieson (1965) reported the X-ray analysis of sporidesmin. Their results are less accurate as photographic methods were used for collecting the data; also the refinement was limited to a few cycles of least squares ($R = 0{\cdot}144$). Disregarding the structural differences between the thiopiperazinedione moieties, the bond lengths agreed reasonably well, apart from the C(6)–C(7) and C(7)–C(8) bonds. In sporidesmin they were 1·45 and 1·41 Å and in sporidesmin G, 1·544 and 1·515 Å respectively. The corresponding bond length in the pyrrolidine ring of gliotoxin (Fridrichsons & Mathieson, 1967) was found to be 1·52 Å.

The angles for the two compounds agree within 5° with the exception of C(8)–C(9)–C(10), which had decreased from 127·4° in sporidesmin to a more acceptable value of 118·9° in sporidesmin G. The three angles at C(7) which in sporidesmin were > 124° had also decreased considerably.

The absolute configuration of sporidesmin was determined by Beecham, Fridrichsons & Mathieson (1966) and that of sporidesmin G was, therefore, assumed to be identical.

Recently Davis & Bernal (1973) determined the structure of *N*,*N*′-dimethyl-3,6-epitetrathio-2,5-piperazinedione (I).



(I)

An exhaustive table of bond lengths and angles found in related compounds was presented by these authors and a similar compilation here would not be justified.

The bond lengths in epitetrathiopiperazinedione of sporidesmin G agree within the experimental error with those found by Davis & Bernal with the exception of the S(4)–C(4) bond, which is longer in sporidesmin G (1·866 and 1·891 Å). This lengthening is possibly significant, and may be due to the fusion at C(4) to the ring *C*.

The angles in the tetrathio-piperazinedione moiety in sporidesmin G are in agreement within 2·0° with the

Table 2. *Vibration tensor components and their e.s.d.'s* (Å² × 10³)

$$\mathrm{T.F.} = \exp\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)\}.$$

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Cl	58 (1)	91 (2)	88 (2)	67 (3)	−48 (3)	−65 (2)
S(1)	54 (1)	88 (2)	137 (2)	0 (4)	−38 (3)	−31 (3)
S(2)	80 (2)	68 (1)	129 (2)	− 4 (3)	−82 (3)	−40 (3)
S(3)	102 (2)	71 (1)	69 (1)	−20 (3)	−83 (3)	1 (3)
S(4)	76 (1)	49 (1)	60 (1)	−43 (2)	−15 (2)	10 (2)
N(1)	58 (4)	66 (4)	63 (4)	26 (7)	2 (7)	−35 (6)
N(2)	36 (3)	37 (3)	49 (3)	−12 (5)	− 2 (5)	12 (5)
N(3)	48 (3)	32 (3)	52 (3)	6 (5)	−10 (6)	16 (5)
O(1)	44 (3)	64 (3)	125 (5)	7 (7)	− 6 (7)	35 (5)
O(2)	73 (3)	54 (3)	96 (4)	56 (6)	−44 (7)	−34 (6)
O(3)	59 (3)	45 (3)	44 (3)	19 (5)	−31 (5)	−11 (5)
O(4)	70 (3)	43 (3)	48 (3)	− 4 (5)	38 (5)	13 (5)
O(5)	83 (4)	38 (3)	77 (4)	−19 (6)	42 (7)	− 3 (5)
O(6)	106 (4)	63 (3)	56 (3)	−10 (6)	−11 (7)	−58 (7)
O(7)	85 (4)	67 (3)	80 (4)	31 (7)	−26 (7)	33 (6)
C(1)	48 (4)	80 (5)	81 (6)	12 (10)	2 (9)	−18 (9)
C(2)	43 (4)	47 (4)	67 (5)	−23 (8)	−18 (8)	2 (7)
C(3)	53 (4)	39 (3)	26 (3)	1 (6)	−11 (6)	− 3 (6)
C(4)	47 (4)	40 (3)	31 (3)	1 (6)	−10 (6)	12 (6)
C(5)	54 (4)	49 (4)	55 (5)	12 (7)	−38 (8)	−24 (7)
C(6)	39 (3)	35 (3)	45 (4)	7 (6)	15 (6)	7 (6)
C(7)	42 (4)	43 (3)	36 (4)	−14 (6)	6 (7)	12 (6)
C(8)	42 (3)	37 (3)	36 (4)	20 (6)	11 (6)	−10 (6)
C(9)	47 (4)	32 (3)	47 (4)	18 (6)	0 (7)	− 3 (6)
C(10)	53 (4)	50 (4)	38 (4)	− 7 (7)	21 (7)	−14 (7)
C(11)	83 (5)	52 (4)	37 (4)	1 (7)	− 2 (8)	−40 (8)
C(12)	56 (4)	65 (5)	47 (4)	40 (8)	− 9 (7)	−63 (8)
C(13)	50 (4)	46 (4)	58 (5)	36 (7)	20 (8)	5 (7)
C(14)	93 (7)	106 (7)	83 (6)	68 (12)	21 (13)	−68 (12)
C(15)	70 (6)	128 (8)	121 (9)	−41 (16)	118 (13)	−28 (13)
C(16)	18 (6)	51 (4)	81 (6)	2 (9)	−30 (11)	7 (9)
C(17)	83 (6)	74 (6)	108 (8)	−20 (11)	80 (13)	2 (10)
C(18)	91 (6)	47 (4)	80 (6)	2 (9)	15 (11)	−38 (9)
C(19)	118 (6)	217 (13)	56 (6)	−94 (17)	2 (13)	12 (18)
C(20)	134 (9)	90 (6)	65 (6)	33 (12)	8 (14)	− 1 (13)
C(21)	141 (10)	104 (8)	142 (11)	65 (17)	−21 (19)	26 (16)
C(22)	327 (23)	271 (18)	140 (13)	−136 (28)	−111 (30)	466 (36)

Table 3. *Fractional coordinates* (× 10^3) *with e.s.d.'s and temperature factors for the hydrogen atoms*

The number of the parent atom is obtained by omitting the last digit. Those marked by an asterisk are attached to the oxygen atoms. The last five atoms of the ether group were not refined.

	x/a	y/b	z/c	B (Å^2)
H(31)*	705 (5)	511 (4)	328 (11)	10·3
H(41)*	730 (4)	598 (3)	−134 (8)	5·1
H(31)	580 (4)	618 (3)	−71 (7)	4·3
H(61)	716 (3)	498 (2)	105 (6)	1·7
H(131)	856 (4)	616 (2)	163 (6)	2·7
H(141)	446 (6)	456 (4)	536 (11)	12·7
H(142)	466 (6)	401 (4)	420 (11)	10·8
H(143)	376 (6)	441 (5)	439 (12)	12·6
H(151)	332 (6)	544 (4)	464 (10)	9·6
H(152)	306 (6)	596 (5)	321 (12)	13·6
H(153)	414 (7)	600 (4)	428 (12)	12·9
H(161)	567 (5)	719 (3)	−94 (10)	8·6
H(162)	492 (5)	711 (4)	−12 (9)	8·4
H(163)	557 (5)	757 (4)	34 (9)	7·6
H(171)	604 (5)	784 (3)	468 (9)	8·1
H(172)	546 (5)	731 (4)	323 (10)	9·8
H(173)	525 (5)	809 (3)	320 (9)	7·3
H(181)	844 (6)	886 (4)	296 (10)	9·3
H(182)	871 (8)	841 (5)	137 (16)	17·3
H(183)	781 (6)	855 (4)	156 (12)	11·3
H(191)	122 (5)	925 (4)	343 (10)	9·3
H(192)	76 (6)	879 (4)	333 (11)	10·8
H(193)	69 (6)	910 (4)	506 (10)	9·9
H(201)	169 (5)	818 (4)	498 (9)	8·5
H(202)	241 (6)	882 (4)	492 (10)	10·8
H(211)	266	758	388	9·0
H(212)	336	815	358	9·0
H(221)	244	752	163	10·0
H(222)	350	726	188	10·0
H(223)	334	793	103	10·0

corresponding values in (I) with a few exceptions. The angles S(1)–C(1)–C(2) and S(4)–C(4)–C(5) are both smaller (104·6 and 105·9°) in sporidesmin G than in (I) (108·6°). On the other hand the angles C(1)–N(1)–C(5) and C(2)–N(2)–C(4) are ~ 11° larger in sporidesmin G. One more angle was found to differ appreciably, C(5)–N(1)–C(14). It is 115·3° in sporidesmin G and 119·0° in (I).

In Table 6 the torsional angles of the ring *C*, *D* and the sulphur bridge are listed. The convention of IUPAC–IUB Commission on Biological Nomenclature (1970) was used. The e.s.d.'s (Huber, 1961) are 0·6° for the ring C bonds, 0·9° for the ring *D* and 0·3° for the bonds with one or two sulphur atoms. The dihedral angles for *N*,*N'*-dimethyl-3,6-epitetrathio-2,5-piperazinedione (Davis & Bernal, 1973) are also presented in Table 6. These values are of the opposite sign, as they were calculated for the enantiomeric configuration. They agree within 16° with the corresponding values for sporidesmin G.

In dithio compounds such as sporidesmin and gliotoxin (Fridrichsons & Mathieson, 1967) small dihedral angles < 20° for the S–S bonds were obtained. However, in tetrathio derivatives, sporidesmin G and (I), the strain was expected to be relieved by a large increase in the torsional angles (Hordvik, 1966; Boyd, 1972). Values of 67 to 107° were observed.

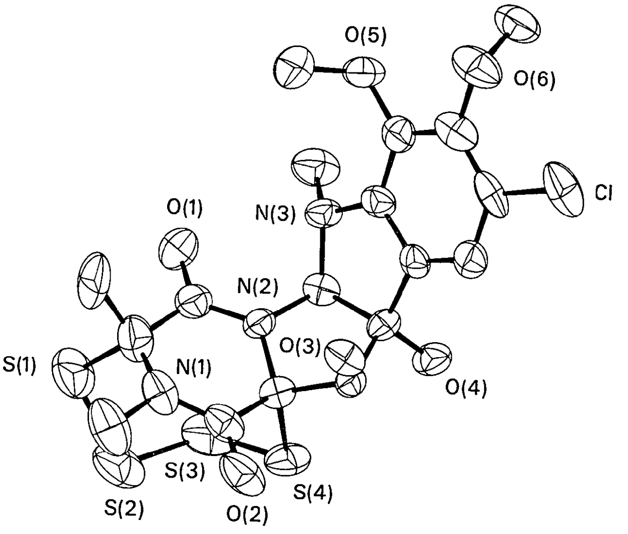
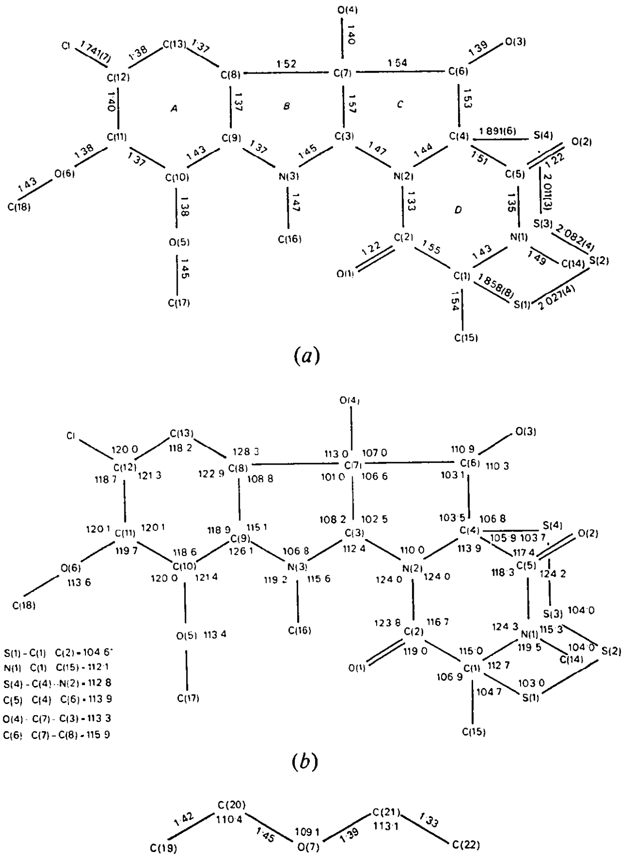


Fig. 1. Projection of the molecule of sporidesmin G showing thermal ellipsoids.



(*a*)

(*b*)

(*c*)

Fig. 2. (*a*) Bond lengths of sporidesmin G. The e.s.d.'s vary from 0·008 to 0·011 Å with the exception of those given in brackets. The e.s.d. for the C(1)–C(15) bond is 0·014. (*b*) Valency angles. Their e.s.d.'s vary between 0·4 and 0·7° giving the average value of 0·6°. (*c*) The molecule of diethyl ether; e.s.d.'s for the central bonds are 0·01 and for the outer 0·02 Å. E.s.d.'s for the angles are 1·0°.

Table 4. *Observed and calculated structure factors* (× 10)

Unobserved reflexions are marked with an asterisk.

K	FO	FC
H= 0, L= 0		
2	1353	1372
4	1824	1828
6	247	229
8	459	453
10	404	388
12	167	158
14	513	509
16	100	91
18	416	411
20	133	134
22	197	199
24	64*	39
H= 0, L= 1		
1	252	262
2	248	190
3	82	55
4	547	562
5	693	674
6	464	435
7	902	833
8	618	593
9	282	281
10	653	642
11	335	330
12	389	379
13	130	121
14	65*	49
15	69*	2
16	106	89
17	172	183
18	113	105
19	129	148
20	114	110
21	78*	52
22	73*	16
23	102	87
24	63*	5
25	57*	7
H= 0, L= 2		
0	1314	1357
1	499	509
2	1347	1271
3	1456	1320
4	1110	1114
5	158	162
6	933	912
7	667	626
8	274	262
9	138	143
10	393	373
11	437	419
12	61*	14
13	236	224
14	67*	49
15	345	340
16	122	129
17	258	274
18	312	317
19	77*	32
20	227	222
21	160	169
22	90	104
23	67*	49
24	95	77
H= 0, L= 3		
1	288	276
2	641	622
3	1142	1072
4	168	161
5	46*	44
6	201	205
7	51*	28
8	556	538
9	346	348
10	260	257
11	629	608
12	435	424
13	67*	44
14	306	310
15	80	81
16	82	95
17	299	291
18	77*	38
19	77*	25
20	75	56
21	73*	56
22	134	132
23	64*	50
24	57*	41
H= 0, L= 4		
0	389	404
1	94	110
2	687	656
3	261	253
4	84	80
5	204	220
6	620	596
7	135	136
8	357	366
9	278	257
10	475	465
11	123	117
12	250	257
13	71*	22
14	315	308
15	121	120
16	181	169
17	77*	26
18	77*	6
19	75*	57
20	138	141
21	82	73
22	64*	56
23	56*	23
H= 0, L= 5		
1	344	327
2	428	414
3	139	143
4	107	102
5	77	53
6	62*	40
7	316	323
8	60*	11
9	421	423
10	70*	34
11	178	160
12	243	247
13	237	233
14	108	99
15	158	151
16	361	361
17	76*	11
18	188	200
19	72*	28
20	149	150
21	63*	28
22	63	76
H= 0, L= 6		
0	83	89
1	348	349
2	209	192
3	163	158
4	173	149
5	307	290
6	149	123
7	114	109
8	72*	64
9	73*	66
10	269	258
11	127	124
12	77*	75
13	201	198
14	248	229
15	76*	65
16	75*	62
17	149	134
18	161	149
19	65	56
20	61*	84
H= 0, L= 7		
1	73*	43
2	98	97
3	73	75
4	74*	43
5	75	65
6	75	52
7	148	150
8	118	109
9	281	265
10	77*	51
11	169	200
12	76*	50
13	76*	36
14	74	67
15	72*	52
16	87	83
17	65	69
18	218	238
H= 0, L= 8		
0	77*	60
1	206	214
2	77*	48
3	77*	52
4	84	100
5	77*	26
6	77	34
7	103	73
8	128	138
9	76*	27
10	82	78
11	93	70
12	96	118
13	69*	41
14	72	70
15	119	109
16	83	93
H= 0, L= 9		
1	82	86
2	116	122
3	74*	66
4	114	117
5	73*	18
6	72*	46
7	71*	33
8	70*	10
9	68*	9
10	66*	32
11	64*	40
12	66	33
13	114	87
H= 0, L= 10		
0	92	114
1	71	67
2	65*	34
3	64*	26
4	63*	40
5	62*	25
6	61*	13
7	59*	30
8	57*	1
H= 1, L= 0		
1	622	657
2	292	325
3	1203	1291
4	277	247
5	167	126
6	1820	1846
7	176	183
8	181	190
9	341	334
10	500	484
11	210	220
12	164	149
13	190	202
14	65*	2
15	491	470
16	315	306
17	249	269
18	225	234
19	228	241
20	77*	81
21	76*	13
22	73*	20
23	69*	40
24	90	61
25	57*	17
H= 1, L= 1		
0	993	1161
1	1686	1945
2	1275	1260
3	791	767
4	532	545
5	825	818
6	631	601
7	457	460
8	401	393
9	328	319
10	507	488
11	346	351
12	326	309
13	118	152
14	78	66
15	69	75
16	215	223
17	124	113
18	265	257
19	312	322
20	179	167
21	158	159
22	80	82
23	69*	24
24	63*	40
H= 1, L= 2		
0	256	251
1	1119	1157
2	485	499
3	814	760
4	1248	1292
5	567	539
6	395	389
7	706	673
8	787	764
9	442	446
10	289	277
11	515	515
12	226	217
13	264	261
14	124	122
15	197	220
16	204	212
17	291	289
18	123	124
19	114	103
20	113	110
21	74	67
22	71*	27
23	90	82
24	119	114
H= 1, L= 3		
0	72	79
1	368	386
2	661	644
3	255	277
4	806	787
5	649	639
6	169	184
7	394	364
8	335	339
9	430	441
10	175	153
11	233	232
12	338	333
13	189	198
14	272	273
15	211	201
16	399	400
17	167	157
18	195	185
19	103	92
20	161	162
21	162	160
22	97	88
23	61*	37
24	57	40
H= 1, L= 4		
0	147	151
1	156	155
2	533	518
3	521	503
4	332	344
5	183	177
6	153	139
7	168	153
8	184	198
9	494	485
10	590	572
11	166	161
12	103	102
13	143	135
14	240	241
15	208	218
16	103	82
17	182	204
18	84	55
19	121	103
20	112	84
21	177	171
22	91	72
23	58*	61
H= 1, L= 5		
0	58*	20
1	378	371
2	156	151
3	369	367
4	60*	52
5	377	367
6	309	319
7	426	436
8	164	151
9	68	60
10	159	160
11	157	157
12	114	112
13	111	88
14	108	85
15	114	102
16	77*	56
17	76*	45
18	74*	55
19	172	174
20	68*	27
21	89	75
22	77	91
H= 1, L= 6		
0	179	187
1	241	247
2	304	303
3	198	162
4	272	276
5	69*	11
6	82	68
7	95	99
8	174	155
9	87	93
10	95	112
11	209	201
12	171	153
13	77*	114
14	77*	43
15	163	155
16	75*	13
17	155	155
18	82	42
19	157	162
20	93	137
H= 1, L= 7		
0	134	136
1	224	256
2	197	208
3	289	282
4	96	105
5	100	133
6	161	153
7	96	73
8	284	273
9	157	151
10	204	235
11	77*	73
12	181	176
13	165	170
14	74*	46
15	111	138
16	75	65
17	71	73
18	81	53
H= 1, L= 8		
0	77*	32
1	154	143
2	129	113
3	77*	47
4	84	55
5	77*	46
6	146	133
7	77*	82
8	76*	43
9	76*	61
10	75*	53
11	103	126
12	71	46
13	69*	39
14	66*	45
15	62*	32
16	58*	26
H= 1, L= 9		
0	95	83
1	142	130
2	75*	39
3	74*	31
4	87	87
5	73*	68
6	72*	36
7	115	96
8	70*	42
9	68*	41
10	88	79
11	63*	44
12	60*	51
13	84	81
H= 1, L= 10		
0	71	98
1	65*	16
2	65*	28
3	64*	44
4	69	43
5	62*	18
6	94	74
7	59*	40
H= 2, L= 0		
0	96	95
1	294	267
2	1229	1182
3	504	540
4	569	553
5	368	381
6	249	245
7	172	149
8	291	297
9	216	207
10	367	389
11	192	200
12	420	453
13	257	235
14	72	54
15	69*	6
16	260	267
17	175	179
18	90	88
19	401	420
20	266	269
21	158	158
22	73	57
23	111	114
24	63*	20
H= 2, L= 1		
0	339	341
1	366	377
2	589	620
3	406	382
4	708	715
5	394	380
6	329	326
7	375	384
8	491	473
9	452	429
10	286	253
11	295	299
12	252	227
13	129	127
14	418	429
15	267	284
16	252	248
17	75*	35
18	96	97
19	251	255
20	153	166
21	75*	66
22	72*	54
23	80	58
24	62*	48
H= 2, L= 2		
0	872	907
1	1225	1383
2	868	938
3	712	734
4	350	338
5	1289	1341
6	491	464
7	661	637
8	535	551
9	604	605
10	408	413
11	322	343
12	90	93
13	223	217
14	272	275
15	114	169
16	87	67
17	261	275
18	77*	44
19	129	133
20	96	91
21	105	113
22	80	61
23	72	54
24	60*	37
H= 2, L= 3		
0	105	115
1	581	604
2	615	635
3	678	665
4	844	818
5	864	865
6	510	487
7	202	207
8	720	717
9	300	306
10	235	215
11	524	516
12	134	112
13	156	160
14	158	157
15	143	151
16	165	161
17	77*	32
18	146	143
19	77	81
20	75*	45
21	102	84
22	146	153
23	108	109
H= 2, L= 4		
0	239	242
1	142	177
2	427	415
3	451	442
4	396	381
5	454	448
6	128	123
7	389	370
8	308	311
9	273	301
10	65*	79
11	323	305
12	233	238
13	310	341
14	74*	23
15	275	289
16	77*	57
17	109	123
18	76*	36
19	95	90
20	112	114
21	68*	40
22	117	113
23	114	114
H= 2, L= 5		
0	139	138
1	274	275
2	352	347
3	285	273
4	118	113
5	474	462
6	168	172
7	197	211
8	466	459
9	276	279
10	271	272
11	155	151
12	234	240
13	316	326
14	123	119
15	77	93
16	119	114
17	83	69
18	74	44
19	95	81
20	124	134
21	62*	51
H= 2, L= 6		
0	66*	54
1	146	159
2	292	316
3	213	213
4	193	185
5	200	188
6	255	253
7	280	285
8	73*	18
9	252	240
10	75*	45
11	76*	38
12	77*	59
13	119	96
14	165	170
15	76*	25
16	74*	32
17	72*	7
18	75	61
19	64*	41
20	59*	15
H= 2, L= 7		
0	123	121
1	161	173
2	140	125
3	187	179
4	213	210
5	171	183
6	96	92
7	127	131
8	77	90
9	188	183
10	77*	45
11	77	82
12	76*	26
13	121	111
14	123	138
15	71	39
16	68*	68
17	64*	10
18	103	105
H= 2, L= 8		
0	77*	39
1	169	157
2	156	159
3	77*	61
4	103	106
5	158	140
6	91	100
7	114	137
8	76*	19
9	75*	58
10	94	94
11	122	118
12	110	116
13	48*	31
14	92	83
15	99	70
16	57*	26
H= 2, L= 9		
0	100	97
1	124	127
2	81	101
3	76*	39
4	123	104
5	103	96
6	72*	31
7	126	123
8	87	74
9	74	76
10	65*	40
11	63*	26
12	75	66
H= 2, L= 10		
0	64*	23
1	64*	40
2	81	87
3	63*	29
4	68	50
5	99	83
6	60*	42
7	68	64
H= 3, L= 0		
1	602	612
2	888	941
3	158	128
4	113	127
5	437	427
6	382	367
7	234	213
8	937	936
9	275	280
10	496	503
11	219	195
12	709	693
13	398	389
14	253	258
15	255	262
16	72*	56
17	75*	30
18	76*	36
19	84	94
20	184	185
21	82	74
22	72*	9
23	171	120
24	62*	16
H= 3, L= 1		
0	574	627
1	478	467
2	405	396
3	1059	1077
4	1276	1298
5	274	254
6	104	120
7	393	365
8	174	174
9	639	596
10	509	492
11	337	327
12	149	140
13	296	293
14	186	196
15	166	159
16	73*	27
17	240	263
18	251	275
19	158	146
20	269	270
21	94	99
22	111	108
23	67	42
24	95	90
H= 3, L= 2		
0	205	209
1	212	203
2	1125	1153
3	707	721
4	516	525
5	727	758
6	513	503
7	564	538
8	381	358
9	117	104
10	284	278
11	325	286
12	590	580
13	370	359
14	69	83
15	466	471
16	309	306
17	76*	62
18	172	186
19	124	121
20	76*	50
21	73*	37
22	70	61
23	65*	69
24	91	84
H= 3, L= 3		
0	452	456
1	366	361
2	497	512
3	631	617
4	438	423
5	930	916
6	474	481
7	730	705
8	521	508
9	337	329
10	61*	39
11	304	299
12	208	213
13	142	128
14	190	209
15	178	170
16	83	93
17	97	97
18	77*	29
19	76*	43
20	74*	29
21	142	157
22	67*	41
23	132	127
H= 3, L= 4		
0	314	295
1	228	222
2	593	592
3	204	196
4	471	472
5	390	375
6	486	469
7	116	132
8	358	369
9	171	192
10	167	171
11	241	238
12	182	174
13	73*	35
14	309	296
15	186	179
16	206	208
17	77	95
18	123	122
19	120	100
20	84	104
21	67	46
22	114	111
H= 3, L= 5		
0	176	180
1	81	76
2	228	238
3	491	504
4	392	389
5	259	250
6	481	494
7	299	301
8	324	308
9	138	95
10	115	102
11	73*	34
12	200	201
13	113	126
14	77*	42
15	84	93
16	77*	78
17	89	80
18	73*	8
19	70*	30
20	66*	41
21	94	63
H= 3, L= 6		
0	354	361
1	68	56
2	284	272
3	87	98
4	378	375
5	70*	61
6	270	262
7	294	305
8	194	202
9	137	142
10	83	81
11	137	133
12	236	236
13	119	107
14	114	96
15	131	115
16	93	74
17	78	59
18	74	46
19	102	117
20	58*	53
H= 3, L= 7		
0	207	194
1	179	183
2	144	58
3	88	85
4	210	223
5	188	204
6	243	246
7	108	138
8	119	122
9	221	214
10	133	125
11	219	209
12	76	84
13	137	138
14	73*	26
15	77	32
16	67*	41
17	69	64
18	58*	32
H= 3, L= 8		
0	192	204
1	84	106
2	103	105
3	77*	54
4	84	75
5	133	133
6	145	145
7	102	109
8	191	189
9	75*	53
10	87	98
11	85	111
12	104	41
13	138	123
14	64*	62
15	60*	48
H= 3, L= 9		
0	114	98
1	114	87
2	151	157
3	73*	64
4	130	115
5	72*	30
6	193	200
7	121	99
8	110	101
9	73	36
10	64*	46
11	67	76
12	62	57
H= 3, L= 10		
0	69	93
1	74	65
2	74	81
3	92	102
4	116	112
5	60*	26
6	58	51
H= 4, L= 0		
0	597	606
1	63*	7
2	346	333
3	870	895
4	518	518
5	473	481
6	212	196
7	474	462
8	457	417
9	53*	17
10	192	199
11	59*	15
12	247	246
13	143	145
14	68*	31
15	127	124
16	119	110
17	185	196
18	97	95
19	366	369
20	76*	13
21	337	316
22	71*	21
23	257	269
24	60*	4
H= 4, L= 1		
0	761	803
1	236	212
2	310	308
3	990	1036
4	453	447
5	805	806
6	261	278
7	485	477
8	379	361
9	281	259
10	298	289
11	718	712
12	299	278
13	565	579
14	97	70
15	210	214
16	181	189
17	293	317
18	241	247
19	124	132
20	76*	49
21	74*	22
22	77	63
23	65*	22
24	70	53
H= 4, L= 2		
0	577	601
1	359	360
2	309	316
3	96	111
4	367	371
5	265	257
6	592	601
7	122	123
8	310	304
9	302	294
10	258	259
11	208	194
12	142	118
13	139	142
14	269	267
15	73*	23
16	164	159
17	113	102
18	234	236
19	108	127
20	75*	90
21	72*	62
22	101	112
23	75	87
24	57*	59
H= 4, L= 3		
0	278	256
1	308	345
2	204	223
3	320	315
4	158	146
5	352	334
6	370	365
7	440	449
8	266	262
9	193	197
10	129	141
11	161	152
12	204	207
13	221	217
14	257	255
15	177	178
16	76*	54
17	212	206
18	119	135
19	76	63
20	87	98
21	70*	42
22	65*	45
23	88	92
H= 4, L= 4		
0	236	246
1	138	136
2	273	285
3	393	379
4	326	331
5	499	486
6	187	204
7	497	500
8	480	482
9	158	126
10	68*	11
11	108	111
12	161	171
13	276	273
14	284	307
15	77*	80
16	221	229
17	103	107
18	107	93
19	73*	59
20	70	58
21	66*	58
22	89	84
H= 4, L= 5		
0	376	396
1	302	326
2	153	152
3	733	771
4	86	85
5	65*	30
6	256	258
7	446	444
8	183	178
9	114	114
10	79	72
11	74*	12
12	210	218
13	102	109
14	77*	47
15	133	139
16	141	128
17	75*	27
18	72*	9
19	75	68
20	64*	22
21	75	83
H= 4, L= 6		
0	157	148
1	87	67
2	176	181
3	140	134
4	118	124
5	175	180
6	305	296
7	80	83
8	266	259
9	172	177
10	295	291
11	119	92
12	221	224
13	77*	64
14	76*	68
15	100	99
16	80	85
17	70*	22
18	98	94
19	61*	28
H= 4, L= 7		
0	328	329
1	282	298
2	175	181
3	112	117
4	76*	28
5	332	351
6	321	343
7	255	250
8	129	136
9	77	65
10	77	80
11	102	122
12	171	172
13	114	115
14	136	150
15	69*	12
16	127	120
17	113	111
H= 4, L= 8		
0	77*	67
1	114	116
2	77*	18
3	77*	71
4	91	108
5	178	205
6	76*	25
7	137	103
8	89	78
9	81	55
10	148	156
11	89	82
12	68*	54
13	66*	28
14	84	78
15	78	71
H= 4, L= 9		
0	98	87
1	92	92
2	72*	36
3	140	141
4	120	111
5	95	89
6	70*	22
7	68*	29
8	107	117
9	123	128
10	79	84
11	59*	42
H= 4, L= 10		
0	61*	9
1	61*	21
2	61*	46
3	85	112
4	59*	68
5	58*	60
H= 5, L= 0		
1	815	805
2	574	592
3	299	295
4	505	503
5	111	108
6	871	881
7	869	889
8	53*	78
9	305	298
10	294	284
11	330	333
12	207	208
13	108	99
14	136	142
15	234	236
16	195	193
17	76*	25
18	77*	55
19	172	190
20	147	129
21	73*	82
22	97	69
23	64*	32
24	81	96
H= 5, L= 1		
0	156	118
1	219	232
2	714	745
3	492	529
4	967	986
5	193	184
6	449	452
7	324	302
8	408	409
9	62	81
10	116	118
11	282	276
12	71	48
13	281	307
14	242	251
15	179	167
16	75	89
17	123	131
18	142	141
19	77*	52
20	89	89
21	72*	78
22	81	62
23	63*	22
H= 5, L= 2		
0	143	130
1	392	385
2	696	697
3	685	689
4	475	476
5	148	175
6	574	561
7	146	136
8	436	423
9	267	254
10	87	88
11	175	159
12	354	352
13	70	63
14	121	113
15	81	98
16	206	221
17	182	193
18	154	157
19	127	120
20	76*	37
21	71*	66
22	66*	13
23	82	35
H= 5, L= 3		
0	212	220
1	435	442
2	189	181
3	353	365
4	676	689
5	125	98
6	62	72
7	273	266
8	384	335
9	89	105
10	146	138
11	168	146
12	121	122
13	148	150
14	74*	27
15	162	154
16	182	176
17	186	195
18	153	148
19	142	145
20	72*	49
21	68	69
22	63	43
23	72	86
H= 5, L= 4		
0	92	96
1	396	431
2	487	516
3	167	146
4	136	134
5	192	177
6	241	242
7	234	223
8	244	238
9	135	142
10	197	207
11	136	140
12	109	92
13	237	245
14	156	177
15	185	202
16	129	140
17	76*	73
18	75*	39
19	85	74
20	68*	40
21	63*	55
22	89	81
H= 5, L= 5		
0	255	243
1	293	305
2	269	271
3	109	115
4	66*	47
5	212	220
6	218	216
7	189	169
8	84	80
9	359	359
10	74*	60
11	157	157
12	127	130
13	285	282
14	119	104
15	137	141
16	169	173
17	74*	13
18	84	83
19	67*	59
20	96	83
H= 5, L= 6		
0	316	339
1	171	157
2	115	130
3	244	237
4	228	247
5	73*	50
6	203	193
7	213	216
8	63	91
9	144	113
10	77*	74
11	119	131
12	77*	57
13	128	135
14	75*	88
15	109	90
16	71	58
17	101	92
18	95	80
19	115	125
H= 5, L= 7		
0	122	113
1	159	152
2	76*	55
3	132	140
4	118	125
5	206	192
6	84	68
7	300	305
8	179	192
9	109	120
10	149	171
11	272	283
12	74	79
13	72	94
14	70*	75
15	123	132
16	63*	31
17	112	98
H= 5, L= 8		
0	77*	28
1	77*	55
2	77*	11
3	97	112
4	102	106
5	144	150
6	75*	75
7	146	159
8	87	73
9	92	80
10	71	46
11	69	81
12	94	83
13	90	129
14	60*	44
H= 5, L= 9		
0	71*	23
1	71*	74
2	110	105
3	83	78
4	99	71
5	81	51
6	163	153
7	126	139
8	87	90
9	62*	39
10	89	92
11	142	157
H= 5, L= 10		
0	118	132
1	59*	52
2	78	94
3	58*	64
H= 6, L= 0		
0	570	586
1	268	267
2	349	346
3	483	485
4	178	183
5	50*	30
6	409	405
7	54*	5
8	145	139
9	459	459
10	174	181
11	184	173
12	130	118
13	374	385
14	170	167
15	145	160
16	131	155
17	77*	42
18	91	72
19	170	182
20	230	247
21	71*	57
22	67*	8
23	86	92
H= 6, L= 1		
0	714	740
1	242	230
2	47*	73
3	409	403
4	270	258
5	377	371
6	615	632
7	258	257
8	621	600
9	196	204
10	422	414
11	327	347
12	173	160
13	278	302
14	134	137
15	165	176
16	76*	48
17	124	125
18	77*	28
19	215	222
20	81	78
21	77	82
22	72	56
23	108	90
H= 6, L= 2		
0	625	617
1	602	626
2	51*	74
3	738	756
4	472	483
5	389	370
6	349	353
7	339	337
8	183	164
9	266	268
10	76	60
11	203	203
12	284	288
13	187	187
14	198	217
15	169	153
16	103	111
17	138	116
18	171	190
19	106	103
20	72	65
21	69*	36
22	70	66
23	63	74
H= 6, L= 3		
0	351	375
1	206	210
2	706	753
3	290	276
4	153	152
5	150	145
6	65	56
7	83	74
8	289	288
9	66*	39
10	238	254
11	250	255
12	269	265
13	209	200
14	75	89
15	119	122
16	77*	48
17	77	63
18	96	96
19	93	91
20	70*	72
21	88	88
22	71	72
H= 6, L= 4		
0	222	222
1	279	292
2	240	226
3	535	537
4	324	325
5	286	300
6	82	83
7	190	190
8	355	346
9	218	226
10	150	172
11	220	232
12	180	165
13	76*	94
14	191	192
15	114	114
16	77*	1
17	193	197
18	73*	36
19	88	88
20	135	132
21	98	97
H= 6, L= 5		
0	115	108
1	184	170
2	175	163
3	68*	86
4	315	310
5	164	183
6	130	134
7	181	177
8	289	281
9	136	140
10	139	155
11	156	144
12	91	102
13	133	138
14	97	71
15	76*	69
16	120	129
17	72*	48
18	69	47
19	64*	48
20	55*	58
H= 6, L= 6		
0	260	286
1	195	182
2	301	319
3	118	129
4	171	172
5	149	152
6	184	167
7	112	103
8	76*	38
9	270	286
10	77*	30
11	150	172
12	161	161
13	135	149
14	169	155
15	72*	41
16	69*	39
17	88	83
18	67	72
H= 6, L= 7		
0	84	91
1	219	217
2	149	144
3	77*	55
4	172	152
5	182	186
6	84	87
7	77*	55
8	157	181
9	187	192
10	95	96
11	100	95
12	134	110
13	70	53
14	117	106
15	64*	27
16	85	88
H= 6, L= 8		
0	76*	3
1	90	82
2	76*	34
3	76*	46
4	95	91
5	95	126
6	74*	44
7	93	98
8	133	152
9	77	35
10	81	63
11	84	89
12	107	93
13	72	60
14	72	58
H= 6, L= 9		
0	69	38
1	135	132
2	75	76
3	68*	26
4	74	89
5	115	118
6	109	117
7	64*	39
8	87	59
9	65*	6
10	72	65
H= 7, L= 0		
1	126	137
2	583	566
3	487	493
4	111	116
5	60	46
6	357	338
7	704	711
8	60*	7
9	265	280
10	325	327
11	527	529
12	70*	62
13	296	297
14	115	105
15	83	101
16	77*	11
17	182	192
18	232	236
19	95	88
20	72*	72
21	68*	46
22	75	77
23	57*	43
H= 7, L= 1		
0	95	69
1	892	906
2	376	376
3	162	146
4	97	101
5	432	422
6	57*	34
7	270	255
8	263	258
9	415	411
10	168	176
11	129	135
12	140	148
13	168	194
14	81	66
15	136	153
16	77*	75
17	142	154
18	76*	19
19	138	147
20	72*	35
21	68	55
22	101	100
H= 7, L= 2		
0	54*	61
1	471	470
2	274	273
3	386	399
4	219	245
5	278	283
6	298	305
7	232	238
8	440	444
9	218	235
10	357	354
11	184	148
12	287	309
13	368	366
14	75	71
15	132	143
16	97	91
17	109	128
18	169	192
19	73	67
20	191	201
21	66*	9
22	101	86
H= 7, L= 3		
0	327	346
1	338	349
2	609	619
3	267	254
4	333	342
5	244	260
6	123	136
7	213	220
8	173	186
9	338	322
10	154	166
11	129	142
12	114	109
13	218	237
14	76	99
15	280	280
16	129	117
17	76*	31
18	190	192
19	71	85
20	85	83
21	74	69
H= 7, L= 4		
0	175	173
1	307	325
2	125	110
3	421	433
4	72	67
5	394	401
6	392	385
7	306	294
8	209	208
9	216	233
10	216	200
11	214	209
12	83	77
13	77*	80
14	176	185
15	77	69
16	76*	28
17	87	81
18	71*	43
19	67*	63
20	93	98
21	88	95
H= 7, L= 5		
0	158	143
1	378	403
2	216	222
3	233	254
4	237	224
5	111	101
6	178	176
7	168	153
8	75*	12
9	151	168
10	180	161
11	140	141
12	126	113
13	114	102
14	76*	56
15	129	129
16	79	52
17	69*	38
18	66*	18
19	95	100
H= 7, L= 6		
0	94	93
1	110	116
2	75*	49
3	198	200
4	274	287
5	117	127
6	85	86
7	141	150
8	209	212
9	109	116
10	77*	73
11	164	160
12	188	199
13	74*	15
14	102	119
15	149	142
16	66*	22
17	84	73
18	56*	29
H= 7, L= 7		
0	97	107
1	77*	69
2	91	81
3	84	83
4	77*	25
5	77*	33
6	197	209
7	160	171
8	148	165
9	111	96
10	93	95
11	102	103
12	147	151
13	132	124
14	65*	12
15	61*	56
H= 7, L= 8		
0	75*	24
1	75*	22
2	82	70
3	153	122
4	74*	51
5	98	63
6	133	126
7	84	101
8	70*	38
9	68	74
10	98	92
11	63	54
12	61*	11
13	95	104
H= 7, L= 9		
0	66*	29
1	66*	50
2	66*	25
3	77	71
4	65*	49
5	63*	47
6	68	41
7	60*	76
8	58*	50
H= 8, L= 0		
0	1734	1775
1	184	198
2	331	375
3	119	122
4	879	910
5	529	522
6	636	644
7	62*	6
8	373	383
9	221	212
10	228	240
11	70	55
12	117	109
13	74*	36
14	76*	37
15	77*	27
16	176	191
17	128	135
18	154	144
19	73*	77
20	70*	17
21	65*	5
22	75	74
H= 8, L= 1		
0	205	201
1	62	59
2	355	363
3	354	344
4	96	101
5	200	198
6	410	417
7	417	421
8	92	84
9	328	330
10	283	286
11	421	428
12	184	181
13	74*	30
14	131	127
15	154	170
16	140	163
17	145	156
18	75	58
19	138	140
20	69*	26
21	71	72
22	59*	37
H= 8, L= 2		
0	492	496
1	186	174
2	65	80
3	144	130
4	154	153
5	62*	66
6	142	139
7	240	257
8	202	214
9	69*	24
10	134	125
11	331	329
12	169	165
13	231	240
14	306	313
15	192	189
16	165	155
17	144	133
18	74*	35
19	78	71
20	67*	30
21	79	79
H= 8, L= 3		
0	295	296
1	278	311
2	178	193
3	180	175
4	356	369
5	152	133
6	133	128
7	363	352
8	264	281
9	251	246
10	73*	46
11	169	160
12	227	229
13	168	181
14	169	168
15	153	147
16	76*	69
17	105	116
18	96	88
19	81	91
20	64*	44
21	78	67
H= 8, L= 4		
0	415	428
1	208	192
2	212	235
3	178	193
4	305	303
5	218	217
6	233	232
7	188	183
8	73*	45
9	124	123
10	294	297
11	160	151
12	212	215
13	109	115
14	188	211
15	76*	74
16	119	145
17	71*	42
18	114	104
19	64*	34
20	59*	61
H= 8, L= 5		
0	219	240
1	72	70
2	107	80
3	103	113
4	185	177
5	74	51
6	195	193
7	154	156
8	113	119
9	188	192
10	124	113
11	146	151
12	77*	55
13	76	71
14	75*	64
15	72	84
16	94	83
17	126	112
18	88	73
19	57*	37
H= 8, L= 6		
0	148	125
1	167	164
2	183	176
3	132	123
4	108	112
5	77*	63
6	91	86
7	189	187
8	77*	19
9	91	62
10	193	200
11	75*	64
12	74*	34
13	120	124
14	116	111
15	66*	23
16	63*	73
17	64	39
H= 8, L= 7		
0	77*	17
1	133	137
2	114	135
3	124	114
4	77*	83
5	132	155
6	117	115
7	171	160
8	100	70
9	73*	39
10	72*	66
11	88	94
12	74	82
13	64*	19
14	94	65
15	57*	18
H= 8, L= 8		
0	86	97
1	73*	63
2	73*	54
3	72	62
4	106	97
5	71*	34
6	76	66
7	86	55
8	84	94
9	82	76
10	112	97
11	70	74
H= 8, L= 9		
0	63*	35
1	63*	57
2	74	61
3	73	65
4	61	51
5	133	133
6	64	35
H= 9, L= 0		
1	436	426
2	394	384
3	61*	73
4	62	33
5	127	147
6	391	391
7	258	255
8	229	227
9	253	276
10	364	371
11	80	74
12	106	116
13	76*	26
14	77*	23
15	231	252
16	77*	3
17	89	66
18	87	84
19	104	84
20	66*	75
21	86	77
H= 9, L= 1		
0	116	134
1	305	294
2	317	305
3	275	266
4	438	435
5	416	434
6	201	204
7	67	42
8	156	153
9	270	264
10	96	97
11	74*	36
12	417	424
13	156	152
14	161	157
15	124	117
16	123	125
17	138	131
18	73*	48
19	82	57
20	83	75
21	60	57
H= 9, L= 2		
0	257	255
1	298	302
2	246	271
3	158	155
4	378	385
5	435	444
6	188	192
7	261	265
8	224	223
9	147	163
10	73	63
11	208	205
12	140	127
13	141	143
14	84	84
15	194	188
16	76*	63
17	115	122
18	71*	45
19	68*	37
20	63*	54
21	58*	43
H= 9, L= 3		
0	66*	48
1	312	329
2	120	102
3	67*	22
4	140	145
5	278	283
6	357	354
7	271	273
8	208	197
9	249	260
10	171	163
11	233	238
12	77	82
13	133	131
14	200	212
15	118	113
16	110	114
17	72*	44
18	69*	11
19	64*	45
20	59	41
H= 9, L= 4		
0	314	316
1	200	203
2	248	255
3	230	232
4	72*	81
5	156	146
6	99	94
7	129	136
8	75*	50
9	201	204
10	149	156
11	185	198
12	182	181
13	138	105
14	147	153
15	119	139
16	111	126
17	68	60
18	115	95
19	88	75
H= 9, L= 5		
0	75*	58
1	111	126
2	149	155
3	262	257
4	75*	9
5	76*	49
6	96	81
7	145	150
8	119	107
9	158	156
10	77*	54
11	103	81
12	76*	29
13	74*	63
14	112	110
15	69*	86
16	94	101
17	88	81
18	57*	46
H= 9, L= 6		
0	146	146
1	77	74
2	154	160
3	114	120
4	229	238
5	109	98
6	204	202
7	77*	21
8	76*	51
9	83	77
10	105	74
11	73*	67
12	96	76
13	107	117
14	106	109
15	68	46
16	69	93
H= 9, L= 7		
0	76*	52
1	76*	69
2	74	75
3	101	106
4	75*	44
5	75*	94
6	74	74
7	73*	16
8	111	93
9	99	68
10	81	64
11	111	110
12	69	76
13	60	77
H= 9, L= 8		
0	70*	39
1	117	113
2	76	80
3	69*	49
4	101	95
5	67*	23
6	135	125
7	65*	53
8	74	48
9	60*	40
10	82	43
H= 9, L= 9		
0	58*	21
1	58*	6
2	58*	47
3	67	31
H= 10, L= 0		
0	174	153
1	227	216
2	72	66
3	376	363
4	227	226
5	109	97
6	160	156
7	104	71
8	397	416
9	73*	52
10	74*	72
11	139	140
12	244	246
13	319	322
14	273	280
15	149	154
16	75	83
17	73*	15
18	70*	20
19	66*	12
20	61*	8
H= 10, L= 1		
0	128	127
1	114	116
2	135	124
3	143	138
4	230	221
5	81	75
6	124	125
7	195	187
8	360	350
9	191	189
10	192	189
11	264	269
12	77*	70
13	77*	59
14	236	213
15	76*	43
16	167	158
17	73*	7
18	69*	17
19	65*	73
20	60*	54
H= 10, L= 2		
0	74	70
1	331	356
2	249	256
3	92	70
4	164	158
5	512	511
6	318	318
7	204	201
8	73*	45
9	307	298
10	336	326
11	145	138
12	220	224
13	77*	35
14	157	153
15	135	143
16	74*	47
17	71*	35
18	68*	21
19	63*	52
20	58*	28
H= 10, L= 3		
0	374	375
1	118	111
2	272	279
3	263	266
4	132	141
5	73*	41
6	154	147
7	105	98
8	215	220
9	76	76
10	252	272
11	223	232
12	77*	22
13	77	64
14	155	164
15	148	148
16	72	72
17	66*	51
18	96	72
19	60*	36
H= 10, L= 4		
0	74*	68
1	74*	63
2	148	138
3	105	91
4	75*	23
5	289	286
6	144	152
7	234	224
8	149	157
9	114	111
10	77*	57
11	77*	57
12	113	125
13	111	86
14	73*	38
15	164	180
16	80	81
17	64*	14
18	106	108
H= 10, L= 5		
0	76*	67
1	76	86
2	224	228
3	141	166
4	104	112
5	133	141
6	207	219
7	129	130
8	103	89
9	119	134
10	76*	59
11	100	75
12	73	31
13	234	256
14	92	101
15	131	121
16	99	95
17	80	54
H= 10, L= 6		
0	77*	91
1	77*	62
2	129	119
3	191	198
4	144	138
5	84	56
6	83	79
7	89	90
8	74*	7
9	73*	16
10	72*	54
11	99	79
12	66*	46
13	65*	14
14	72	33
15	57*	20
H= 10, L= 7		
0	81	63
1	87	58
2	74*	36
3	103	73
4	138	136
5	102	81
6	90	82
7	88	74
8	68	57
9	111	97
10	76	61
11	67	70
12	64	21
H= 10, L= 8		
0	78	68
1	66*	67
2	65*	63
3	65*	69
4	64*	26
5	65*	64
6	67	70
7	75	78
8	77	28
H= 11, L= 0		
1	93	121
2	305	302
3	126	123
4	115	122
5	195	208
6	394	385
7	76*	55
8	125	116
9	76*	83
10	267	274
11	77*	46
12	379	399
13	91	76
14	144	146
15	74*	30
16	72	56
17	69*	41
18	65*	19
19	61*	4
H= 11, L= 1		
0	393	388
1	125	141
2	109	134
3	95	75
4	316	316
5	97	111
6	173	197
7	347	344
8	106	102
9	145	208
10	205	206
11	212	212
12	124	124
13	145	141
14	107	111
15	137	148
16	79	79
17	97	95
18	87	76
19	60*	27
H= 11, L= 2		
0	120	128
1	85	96
2	167	150
3	129	114
4	206	212
5	74*	25
6	383	368
7	75*	36
8	117	112
9	145	143
10	275	267
11	119	106
12	194	202
13	90	95
14	95	73
15	173	185
16	133	128
17	67*	42
18	79	89
19	93	87
H= 11, L= 3		
0	114	94
1	74*	45
2	132	121
3	249	251
4	142	149
5	236	230
6	217	228
7	145	157
8	194	190
9	176	152
10	119	134
11	77*	53
12	132	133
13	75*	81
14	73	49
15	95	88
16	67*	29
17	150	171
18	70	61
H= 11, L= 4		
0	113	117
1	240	252
2	238	255
3	156	150
4	194	208
5	103	123
6	77*	33
7	97	112
8	77*	68
9	84	74
10	113	135
11	75*	26
12	172	167
13	72	50
14	159	151
15	107	103
16	63*	24
17	58	36
H= 11, L= 5		
0	119	105
1	97	88
2	109	117
3	154	162
4	251	256
5	114	134
6	236	208
7	170	174
8	101	93
9	75*	32
10	114	105
11	72*	27
12	70*	82
13	67*	72
14	64*	53
15	60*	60
H= 11, L= 6		
0	169	186
1	112	101
2	89	86
3	139	133
4	82	92
5	100	88
6	136	129
7	103	113
8	71*	60
9	103	55
10	68*	12
11	105	90
12	63*	23
13	75	58
H= 11, L= 7		
0	70*	31
1	70*	13
2	70*	47
3	70*	31
4	69*	18
5	86	80
6	67*	52
7	65*	28
8	63*	46
9	95	75
10	64	75
H= 11, L= 8		
0	61*	49
1	60*	52
2	66	59
3	59	69
4	67	69
5	57*	33
H= 12, L= 0		
0	150	145
1	73	63
2	74*	4
3	88	75
4	182	187
5	154	161
6	162	188
7	76*	23
8	181	176
9	77*	8
10	77*	2
11	119	125
12	102	110
13	106	119
14	114	108
15	78	69
16	68*	31
17	95	97
18	60	23
H= 12, L= 1		
0	155	143
1	155	147
2	74*	46
3	233	228
4	142	129
5	75*	79
6	76	98
7	450	446
8	200	214
9	114	108
10	84	89
11	77*	70
12	152	144
13	125	107
14	46	62
15	71	63
16	67*	69
17	121	118
18	59*	15
H= 12, L= 2		
0	171	165
1	138	132
2	75*	57
3	89	95
4	179	179
5	304	300
6	153	163
7	133	129
8	109	95
9	138	153
10	146	149
11	90	77
12	95	92
13	99	110
14	164	184
15	92	70
16	65*	16
17	61	56
H= 12, L= 3		
0	183	198
1	163	146
2	76*	77
3	160	148
4	77*	69
5	142	150
6	77*	66
7	241	244
8	109	94
9	188	189
10	90	79
11	157	175
12	73*	56
13	71	23
14	169	163
15	66*	55
16	73	36
17	57*	15
H= 12, L= 4		
0	109	126
1	77*	78
2	146	148
3	77*	70
4	142	150
5	158	161
6	84	77
7	76*	52
8	102	104
9	111	118
10	74*	32
11	72*	41
12	77	29
13	68	101
14	64*	74
15	61*	38
H= 12, L= 5		
0	76*	27
1	234	240
2	76	72
3	144	135
4	131	110
5	89	56
6	138	143
7	104	93
8	73*	10
9	106	98
10	76	52
11	74	61
12	65*	49
13	95	81
14	58*	20
H= 12, L= 6		
0	153	147
1	113	91
2	72	51
3	72*	83
4	120	97
5	109	99
6	162	152
7	97	70
8	127	129
9	65*	53
10	68	54
11	60*	38
H= 12, L= 7		
0	66*	33
1	134	121
2	65*	69
3	71	57
4	103	82
5	63	55
6	61*	66
7	70	62
8	63	48
H= 13, L= 0		
1	113	100
2	76*	1
3	76*	8
4	250	205
5	182	181
6	218	213
7	133	106
8	91	98
9	128	130
10	76*	42
11	187	177
12	74*	20
13	78	67
14	69*	5
15	98	83
16	62*	65
17	85	48
H= 13, L= 1		
0	118	92
1	84	82
2	239	252
3	114	120
4	228	233
5	97	98
6	103	91
7	169	160
8	77	82
9	76*	75
10	76*	53
11	153	154
12	157	159
13	135	154
14	68	71
15	65	51
16	61*	33
17	57*	56
H= 13, L= 2		
0	119	123
1	142	141
2	137	136
3	77*	19
4	77*	22
5	150	147
6	91	83
7	77*	46
8	168	192
9	201	215
10	106	99
11	76*	26
12	91	83
13	69*	23
14	79	54
15	69	48
16	65	55
H= 13, L= 3		
0	77*	5
1	124	107
2	124	136
3	169	161
4	109	94
5	109	104
6	202	208
7	76*	36
8	117	136
9	74	26
10	85	72
11	111	106
12	82	56
13	103	100
14	63	53
15	59*	41
H= 13, L= 4		
0	76*	5
1	76*	75
2	76	84
3	127	122
4	107	107
5	89	107
6	82	59
7	144	137
8	73	42
9	78	86
10	88	65
11	165	153
12	100	54
13	83	47
14	58*	72
H= 13, L= 5		
0	128	121
1	76	80
2	109	74
3	113	132
4	73*	22
5	147	165
6	71	37
7	132	108
8	68*	11
9	89	73
10	99	80
11	61*	39
12	64	65
H= 13, L= 6		
0	140	141
1	68*	64
2	121	115
3	113	100
4	73	38
5	83	93
6	66*	17
7	79	67
8	66	53
9	78	68
H= 13, L= 7		
0	59*	29
1	118	118
2	59*	61
3	124	129
4	57*	44
H= 14, L= 0		
0	77*	70
1	77	74
2	77*	78
3	77	74
4	77*	10
5	103	100
6	118	101
7	76*	91
8	106	65
9	81	73
10	175	175
11	78	73
12	82	71
13	84	52
14	63	48
15	59*	4
H= 14, L= 1		
0	142	127
1	114	102
2	185	190
3	165	170
4	77	50
5	197	190
6	113	107
7	76	82
8	95	78
9	99	74
10	125	129
11	95	80
12	110	110
13	141	125
14	96	69
15	107	105
H= 14, L= 2		
0	137	124
1	168	184
2	178	181
3	128	104
4	84	77
5	76*	21
6	101	95
7	75*	58
8	172	170
9	86	81
10	71*	53
11	69*	22
12	133	122
13	63*	74
14	80	66
H= 14, L= 3		
0	76*	31
1	76*	41
2	197	181
3	75*	35
4	168	140
5	94	85
6	155	157
7	80	43
8	120	127
9	70*	48
10	91	93
11	66	30
12	94	90
13	60	72
H= 14, L= 4		
0	74*	80
1	143	163
2	93	71
3	73*	37
4	177	164
5	111	101
6	71*	31
7	69*	49
8	86	80
9	83	73
10	75	50
11	67	57
12	56*	34
H= 14, L= 5		
0	69*	53
1	69*	70
2	111	93
3	68*	7
4	85	84
5	89	86
6	65*	76
7	64	48
8	120	110
9	59*	68
H= 14, L= 6		
0	127	112
1	96	93
2	61*	47
3	67	49
4	96	82
5	74	32
6	80	88
H= 15, L= 0		
1	83	80
2	187	191
3	164	168
4	100	85
5	74*	37
6	80	64
7	165	161
8	71*	22
9	69*	24
10	67*	10
11	216	210
12	118	131
13	112	122
H= 15, L= 1		
0	75*	29
1	106	105
2	75*	40
3	149	132
4	74	63
5	74*	72
6	73*	31
7	72*	5
8	71*	25
9	69*	42
10	67*	39
11	76	56
12	87	36
13	78	78
H= 15, L= 2		
0	74*	33
1	74*	52
2	115	117
3	87	71
4	176	163
5	92	81
6	166	160
7	70*	15
8	69*	57
9	90	51
10	142	130
11	84	67
12	65	56
H= 15, L= 3		
0	137	142
1	116	105
2	79	55
3	71*	42
4	78	58
5	94	64
6	131	116
7	117	96
8	114	132
9	164	159
10	61	48
11	58*	14
H= 15, L= 4		
0	122	124
1	110	88
2	75	56
3	148	147
4	90	61
5	121	122
6	64*	49
7	119	126
8	61*	85
9	78	70
H= 15, L= 5		
0	88	67
1	97	95
2	96	99
3	67	37
4	60*	56
5	65	52
6	73	71
H= 16, L= 0		
0	96	98
1	71*	62
2	135	106
3	89	96
4	185	141
5	69*	26
6	68*	7
7	66*	4
8	65	53
9	84	97
10	60*	22
11	67*	2
H= 16, L= 1		
0	71*	72
1	118	97
2	77	51
3	77	78
4	69*	85
5	68*	57
6	79	61
7	102	89
8	86	72
9	62*	40
10	88	62
H= 16, L= 2		
0	69	74
1	98	91
2	81	74
3	94	102
4	100	106
5	66*	47
6	65*	32
7	98	94
8	103	86
9	59*	48
H= 16, L= 3		
0	72	59
1	66*	49
2	93	72
3	65*	36
4	64	45
5	63*	21
6	99	106
7	60*	48
8	58*	24
H= 16, L= 4		
0	72	70
1	136	137
2	72	61
3	80	86
4	105	106
5	68	65
H= 17, L= 0		
1	64*	61
2	64	44
3	63*	67
4	62*	16
5	125	100
6	60*	31
7	78	78
H= 17, L= 1		
0	110	126
1	64*	45
2	63*	22
3	74	82
4	67	37
5	90	90
6	59*	44
7	57*	9
H= 17, L= 2		
0	67	56
1	61*	22
2	77	85
3	60*	43
4	60	65
5	113	99
H= 17, L= 3		
0	58*	17
1	68	72
2	57*	20

Table 5. *Agreement summary*

2152 observed reflexions, $|F_o \max| = 182{\cdot}4$.

Limits	Number
$|\Delta F|/|F_o| \le 2R$, or $|\Delta F| \le 1|F_{\rm th}|$	2146
$2R < |\Delta F|/|F_o| \le 3R$, or $1|F_{\rm th}| < |\Delta F| \le 2|F_{\rm th}|$	5
$3R < |\Delta F|/|F_o| \le 4R$, or $2|F_{\rm th}| < |\Delta F| \le 3|F_{\rm th}|$	1

667 unobserved reflexions, $|F_c \max| = 11{\cdot}1$.

$|F_c| \le 1{\cdot}0|F_{\rm th}|$	596
$1{\cdot}0|F_{\rm th}| < |F_c| \le 1{\cdot}5|F_{\rm th}|$	70
$1{\cdot}5|F_{\rm th}| < |F_c| \le 2{\cdot}0|F_{\rm th}|$	1

$|F_{\rm th}|$ = threshold amplitude = 3·6 to 7·7.
Final $R = 0{\cdot}057$, omitting the unobserved reflexions.

Table 6. *Torsional angles*

Ring *C* of sporidesmin G.

N(2)–C(3)–C(7)–C(6)	4·9°
C(3)–C(7)–C(6)–C(4)	17·1
C(7)–C(6)–C(4)–N(2)	−33·4
C(6)–C(4)–N(2)–C(3)	39·5
C(4)–N(2)–C(3)–C(7)	−27·6

Ring *D* and the sulphur bridge

	Sporidesmin G	*N*,*N*′-Dimethyl-3,6-epitetrathio-2,5-piperazinedione
C(1)–C(2)–N(2)–C(4)	24·0°	−8·7°
C(4)–C(5)–N(1)–C(1)	9·2	−8·7
C(2)–N(2)–C(4)–C(5)	−31·9	25·6
C(5)–N(1)–C(1)–C(2)	−17·4	25·6
N(2)–C(4)–C(5)–N(1)	14·2	−16·8
N(1)–C(1)–C(2)–N(2)	1·1	−16·8
C(2)–C(1)–S(1) –S(2)	83·1	−87·3
S(3) –S(4) –C(4)–C(5)	86·4	−87·3
C(1)–S(1) –S(2) –S(3)	−67·4	68·6
S(2) –S(3) –S(4) –C(4)	−71·7	68·6
S(1) –S(2) –S(3) –S(4)	107·1	−105·3
N(1)–C(1)–S(1) –S(2)	−42·5	42·8
S(3) –S(4) –C(4)–N(2)	−38·8	42·8

The results of the examination of the planarity of the different portions of sporidesmin G are presented in Table 7. The benzene ring *A* shows some distortion from planarity, the atoms C(10) and C(11) being at ~0·02 Å and on the opposite sides of the plane calculated for the six atoms. It was found, however, to be much more planar than the ring *A* in sporidesmin and the deviations of Cl, O(5) and O(6) are also considerably smaller.

Both five-membered rings are envelope-shaped, but only the four atoms of the ring *B* can be considered as planar. The distance of C(3) from the plane of the remaining atoms in the ring *B* is 0·03 Å, but the deviation of C(4) from the plane of the ring *C* is 0·54 Å. The ring *B*, is, therefore, considerably flattened. In sporidesmin the distances of the C(3) atom in the ring *B* and of the C(6) atom in the ring *C* were 0·3 Å from the planes calculated for the other four atoms.

The C(17) and C(18) atoms in sporidesmin G are in *trans* conformation, but in sporidesmin they are *cis* with respect to each other.

There is an appreciable difference in the conformations of the two carbonyl groups (see Table 7). One is planar (plane 4) and the other (plane 5) shows significant deviations from planarity. The two peptide portions of the ring *D* are not planar and this is reflected in the values of the torsional angles for the C(5)–N(1) and C(2)–N(2) bonds, which are 9·2 and 24·0° respectively (Table 6).

The diketopiperazine ring approaches the twist boat conformation with the largest torsional angle being 32°. A plane for five atoms was calculated (plane 6 in Table 7) and it was found that the atom C(4) is situated at a distance of 0·21 Å from that plane and on the same side as the sulphur chain, whereas the nitrogen atoms are at ~0·15 Å below that plane. The X-ray analyses of a number of related compounds revealed that the strain due to the substitution influences the conformation of the diketopiperazine ring. Cyclo-D-Ala-L-Ala was found to be nearly planar (Sletten, 1970), cyclo-L-Pro-L-Leu (Karle, 1972), gliotoxin and sporidesmin have boat conformations, whereas twist boat conformations were observed in LL-S88α (Cosulich, Nelson & Van den Hende, 1968) and in cyclo-L-Ala-L-Ala (Sletten, 1970).

The tetrathiopiperazinedione moiety of sporidesmin G projected perpendicularly to the N(1)–C(5) and N(2)–C(2) bonds is shown in Fig. 3. The S(4)–C(4) bond is more tilted upwards than the corresponding C(1)–S(1) bond. It seems that the proximity of the hydroxyl group, O(4), causes this displacement of the S(4) atom, as the distance S(4)···O(4) is 3·35 Å.

The reaction of sporidesmin to form sporidesmin G and the biosynthesis of sporidesmin G by *P. chartarum* proceed stereospecifically with respect to sulphur. The sulphur atoms in tetrathio compounds are oriented towards the nitrogen atoms of the piperazinedione ring and the S···N intramolecular distances, listed in Table 8, are appreciably shorter than the sum of van der Waals radii (3·35 Å). The bond lengths in 2,5-piperazinedione (Degeilh & Marsh, 1959) and in that ring in sporidesmin G are normal for the amide group (Corey & Pauling, 1953). The considerable shortening of the C–N bonds (1·33 and 1·35 Å) in amide groups in sporidesmin G indicates partial double-bond character and hence the nitrogen atoms must have an increment of positive charge. The sulphur atoms are therefore more attracted by the nitrogen atoms than by the carbon atoms of the carbonyl groups. Hence we suggest that the unique stereochemistry between sulphur and nitrogen atoms found in the tetrathio compounds is a consequence of this electrostatic attraction.

In support of this explanation is the fact that the bond between the central donor S atoms of the thio bridge is appreciably lengthened (2·082 Å). In this connexion it is also interesting that LaLonde, Wong & Das (1973) observed a strong band at 290–300 nm in β-thiohemiaminals. The authors attributed it to the intramolecular interaction between the sulphur and the immonium ion. An absorption band was also observed in that region of the ultra violet in sporidesmin G (Francis *et al.*, 1972).

The distance O(2)···O(3) in sporidesmin was 2·82 Å indicating an intramolecular hydrogen bond. In sporidesmin G this distance increased to 2·958 (8) Å.

Two hydrogen bonds hold the molecules together, one between the molecules of sporidesmin G and the other between those of sporidesmin G and diethyl ether. The first one O(3)–H···O(4) is shown in Fig. 4. Reproduced through the operation of the twofold screw axis, it gives rise to a hydrogen bond with a third molecule above and thus to a hydrogen-bonded spiral of sporidesmin G molecules, parallel to the *c* axis. The other hydrogen bond, O(4)–H···O(7), is drawn in Fig. 5.

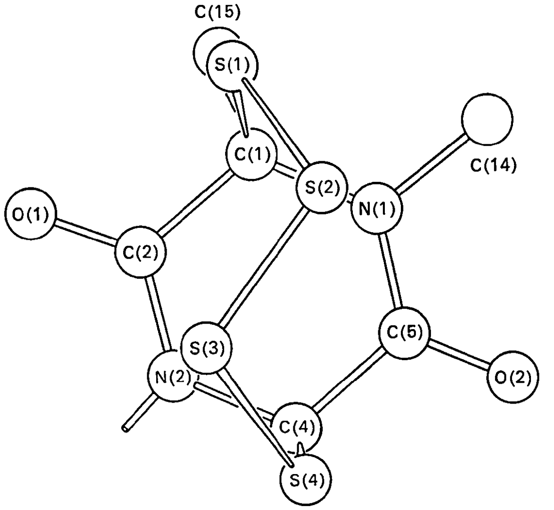


Fig. 3. The tetrathiopiperazinedione moiety.

Table 8. *Short intramolecular distances between the sulphur atoms and atoms of the piperazinedione ring*

S(1)···O(1)	3·089 (6) Å
S(4)···O(2)	3·145 (6)
S(2)···N(1)	3·162 (7)
S(3)···N(2)	3·175 (6)
S(2)···C(1)	3·041 (9)
S(3)···C(4)	3·068 (7)
S(2)···C(5)	3·420 (8)
S(3)···C(2)	3·229 (8)

The pertinent data are:

	O···O	H···O
O(3)–H(31)···O(4)	2·78 Å	2·18 Å
O(4)–H(41)···O(7)	2·76	2·02

O–H	<C–O–H	<O–H···O
0·62 Å	115·1°	164·1°
0·74	112·3	171·9

Fig. 5 also shows that excluding the sulphur bridge atoms, the skeleton of sporidesmin G is roughly V shaped. The planes of the two halves of the molecule meet at the C(3)–C(7) bond with the dihedral angle of 60°.

All the intermolecular contacts are normal. Only three approaches were found to be slightly shorter than

Table 7. *Least-squares planes*

Plane 1 (ring *A*)	Δ	Plane 2 (ring *B*)	Δ	Plane 3 (ring *C*)	Δ	Plane 4 (carbonyl group)	Δ	Plane 5 (carbonyl group)	Δ	Plane 6 (ring *D*)	Δ
C(8)	0·003 Å	N(3)	−0·004	N(2)	−0·013	O(2)	−0·001	N(2)	−0·008	O(1)	−0·006
C(9)	0·011	C(7)	0·004	C(3)	0·030	N(1)	−0·001	O(1)	−0·011	O(2)	−0·003
C(10)	−0·022	C(8)	−0·009	C(6)	0·019	C(4)	−0·001	C(1)	−0·016	C(1)	0·000
C(11)	0·018	C(9)	0·010	C(7)	−0·029	C(5)	0·004	C(2)	0·043	C(2)	0·010
C(12)	0·001	C(3)*	−0·031	C(4)*	0·540					C(5)	0·004
C(13)	−0·012									N(1)*	−0·177
Cl*	0·015									N(2)*	−0·122
N(3)*	0·008									C(3)*	−0·264
O(5)*	−0·032									C(4)*	0·214
O(6)*	−0·004									C(14)*	−0·332
C(7)*	0·039										
r.m.s.d. = 0·014 $\chi^2 = 22·9$		r.m.s.d. = 0·008 $\chi^2 = 5·6$		r.m.s.d. = 0·025 $\chi^2 = 65·0$		r.m.s.d. = 0·002 $\chi^2 = 0·5$		r.m.s.d. = 0·024 $\chi^2 = 44·9$		r.m.s.d. = 0·006 $\chi^2 = 3·8$	

Equations of the planes are:

	a	*b*	*c*	*m*
1	0·2948	0·3594	−0·8854	7·1178
2	0·2983	0·3728	−0·8787	7·3607
3	−0·1308	−0·5362	−0·8339	−8·4517
4	−0·4887	−0·5337	−0·6902	−10·8661
5	−0·3160	−0·4935	−0·8103	−9·4217
6	−0·3740	−0·4851	−0·7905	−9·6562

where $aX+bY+cZ=m$; X, Y and Z are coordinates in Å.

* Atoms excluded from the calculation of the plane.

the sum of the corresponding van der Waals radii, but these deviations are not significant, as their e.s.d.'s are ~0·12 Å. These close contacts are: S···H, 2·93 Å; O···H, 2·46 Å and H···H, 2·36 Å.

Grateful acknowledgement is made to Dr F. R. Ahmed, Dr C. P. Huber and Mrs M. E. Pippy for the use of their programs for the IBM/360 system (Ahmed, Hall, Pippy & Huber, 1966). Thanks are also due to Mrs H. Sheppard for technical assistance and to Dr O. E. Edwards, Dr R. T. LaLonde from Syracuse University and Dr J. Hudec from the University of Alberta for helpful discussions.

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. IUCr *World List of Crystallographic Computer Programs*. 2nd ed. Appendix, p. 52.

Beecham, A. F., Fridrichsons, J. & Mathieson, A. McL. (1966). *Tetrahedron Lett.* pp. 3131–3137.

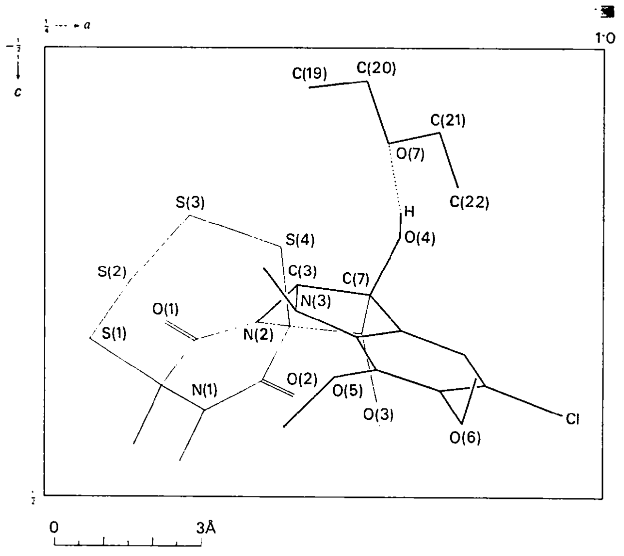


Fig. 5. View of the hydrogen bond between the molecule of sporidesmin G and diethyl ether along the *b* axis.

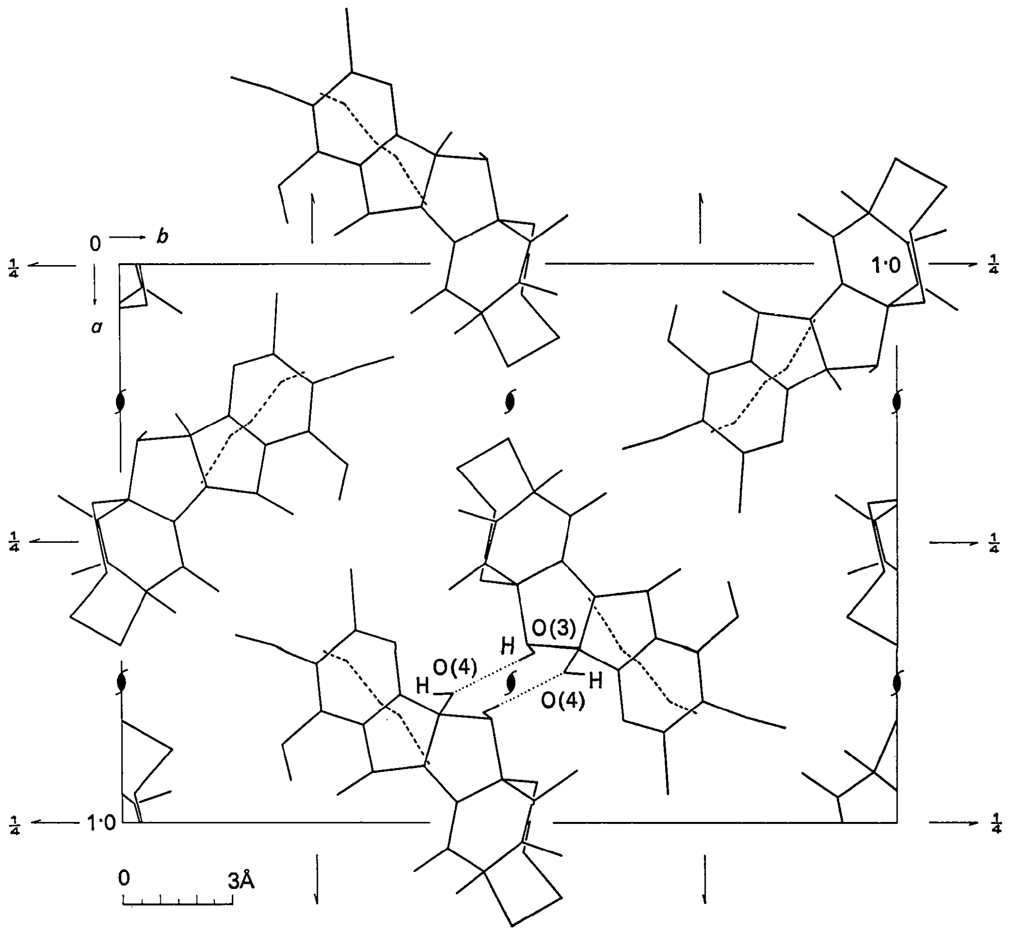


Fig. 4. Packing of the molecules projected down the *c* axis. The ether molecule is drawn with broken lines and hydrogen bonds with dotted lines.

Boyd, D. B. (1972). *J. Amer. Chem. Soc.* **94**, 8799–8804.
Corey, R. B. & Pauling, L. (1953). *Proc. Roy. Soc.* **B141**, 10–20.
Cosulich, D. B., Nelson, N. R. & Van den Hende, J. H. (1968). *J. Amer. Chem. Soc.* **90**, 6519–6521.
Davis, B. R. & Bernal, I. (1973). *Proc. Natl. Acad. Sci. U.S.* **70**, 279–283.
Degeilh, R. & Marsh, R. E. (1959). *Acta Cryst.* **12**, 1007–1014.
Francis, E., Rahman, R., Safe, S. & Taylor, A. (1972). *J. Chem. Soc. Perkin* I, pp. 470–472.
Fridrichsons, J. & Mathieson, A. McL. (1965). *Acta Cryst.* **18**, 1043–1052.
Fridrichsons, J. & Mathieson, A. McL. (1967). *Acta Cryst.* **23**, 439–448.
Hordvik, A. (1966). *Acta Chem. Scand.* **20**, 1885–1891.
Huber, P. J. (1961). *Helv. Chim. Acta*, **44**, 2032–2033.
International Tables for X-ray Crystallography. (1962). Vol. III. Birmingham: Kynoch Press.
IUPAC–IUB Commission on Biological Nomenclature (1970). *J. Mol. Biol.* **52**, 1–17.
Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794 revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
Karle, I. L. (1972). *J. Amer. Chem. Soc.* **94**, 81–84.
Karle, J. & Hauptman, H. (1956). *Acta Cryst.* **9**, 635–651.
LaLonde, R. T., Wong, C. F. & Das, K. C. (1973). *J. Amer. Chem. Soc.* **95**, 6342–6349.
Przybylska, M., Gopalakrishna, E. M., Taylor, A. & Safe, S. (1973). *J. C. S. Chem. Commun.* pp. 554–555.
Sletten, E. (1970). *J. Amer. Chem. Soc.* **92**, 172–177.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement.* London: The Chemical Society.
Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

Acta Cryst. (1974). B30, 605

Identification d'un Nouvel Hydrate du Nitrate de Calcium $Ca(NO_3)_2.2H_2O$ β

Par André Leclaire

Laboratoire de Cristallographie-Minéralogie, Groupe de Cristallographie et Chimie du Solide, U.E.R. des Sciences, Université,* 14032 *Caen, France*

(*Reçu le* 13 *juillet* 1973, *accepté le* 22 *octobre* 1973)

β-$Ca(NO_3)_2.2H_2O$, monoclinic, $C2/c$, $a=7{\cdot}79$ (1), $b=6{\cdot}88$ (1), $c=12{\cdot}22$ (1) Å, $\beta=90{\cdot}0$ (3)°, $Z=4$, $D_x=2{\cdot}03$ g cm^{-3}. The material was crystallized from a supersaturated aqueous solution. The structure consists of layers parallel to the *ab* plane, held together by hydrogen bonds. The Ca coordination is 10.

Introduction

De nombreuses études du diagramme de solubilité du nitrate de calcium dans l'eau mettent en évidence un dihydrate du nitrate de calcium (Lescoeur, 1890; Basset & Taylor, 1912; Ewing, Krey, Law & Lang, 1927; Sieverts & Petzold, 1933). Dans le cadre d'une étude de diverses propriétés des hydrates du nitrate de calcium (Leclaire & Monier, 1970) nous avons isolé, en plus du dihydrate décrit dans la littérature, une nouvelle forme à $2H_2O$ du nitrate de calcium que nous appelons la forme β.

Ce composé a été obtenu en laissant cristalliser une solution sursaturée de nitrate de calcium dans l'eau à une température comprise entre 47° et 49°. Au bout d'un mois environ, apparaissent des cristaux transparents qui ressemblent à des plaquettes hexagonales. Ces cristaux sont délimités par: le pinacoïde $\{001\}$ dont les grandes dimensions conduisent au faciès en plaquettes, et les prismes $\{101\}$, $\{110\}$, $\{111\}$ et $\{11\bar{1}\}$. Habituellement, seules les trois premières formes se manifestent et ce n'est que sur les très gros cristaux que les deux dernières apparaissent.

Sa formule chimique a été déterminée par le dosage volumétrique du calcium à l'EDTA. Les cristaux sont instables et blanchissent rapidement hors de leur solution de telle sorte que les clichés de diffraction des rayons X par un monocristal scellé dans un tube en verre de Lindemann ne présentent plus que des anneaux de Debye–Scherrer après 24 h d'enregistrement. Le produit issu de la transformation a la même formule pondérale que le dihydrate; nous pouvons en conclure que la variété β se transforme de façon irréversible en un dihydrate plus stable.

Le spectre de diffraction des rayons X présente les extinctions systématiques, $h+k=2n+1$ dans hkl, $h=2n+1$ et $l=2n+1$ dans $h0l$, compatibles avec les groupes spatiaux Cc et $C2/c$.

Détermination de la structure

En raison des difficultés d'obtention des cristaux et de la rapidité avec laquelle ils se décomposent, nous avons

---

* Equipe de Recherche associée au CNRS n° 305.