4. Conclusion

The present computations provide a quantitative explanation for the 'unusual' conformation adopted for adrenaline in the crystal of its hydrogen tartrate complex in terms of the strong stabilization of the crystal lattice which overcomes by far the loss of conformational energy with respect to the theoretically most stable conformer of the free molecule. Conceptionally the situation is thus analogous to that encountered in our previous study of the effect of the crystal environment on the stacking pattern of adenines (Caillet & Claverie, 1974): namely, the optimal geometry of the *isolated* subunit [binary complex in Caillet & Claverie (1974) or the free molecule in the present case] need not necessarily be identical to the optimal geometry in a crystal, corresponding to the interaction of such subunits. These examples stress the necessity of explicitly taking into account environmental factors in cases in which the experimental results are at variance with predictions referring to free molecules and show also the possibility of arriving at an agreement between the two aspects with the presently available methodologies and computational techniques.

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The Crystal Structure of *O*-Ethyl *S*-(11-Carboxyundecyl)dithiocarbonate

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O-Ethyl *S*-(11-carboxyundecyl)dithiocarbonate ($C_{15}H_{28}S_2O_3$) is triclinic ($P\overline{1}$) with $a=7\cdot534$, $b=4\cdot797$, $c=25\cdot304$ Å, $\alpha=90\cdot83$, $\beta=90\cdot72$ and $\gamma=79\cdot71°$. The bond distances and angles agree very well with those reported earlier for the homologue with a shorter carbon chain (C5). The conformations are also very similar in the two compounds. The ethyl end of one molecule just reaches S(2) of a neighbouring one. This results in a packing with only small regions of lateral hydrocarbon chain packing. The chain arrangement cannot be described by any known subcell.

Introduction

In a previous report from this laboratory the crystal structure of a hexanoic acid with an ethyldithiocarbonate group in the ω position was described (HES) (Abrahamsson & Innes, 1974). The present study has been undertaken to make possible a comparison with a homologue with a longer hydrocarbon chain, *i.e.* dodecanoic acid (DOS).

Crystal data

$C_{15}H_{28}S_2O_3$, triclinic, $a=7\cdot534$ (6), $b=4\cdot797$ (4), $c=25\cdot304$ (14) Å, $\alpha=90\cdot83$ (4), $\beta=90\cdot72$ (4), $\gamma=79\cdot71$ (4)°, $V=899\cdot57$ Å^3, M.W. 320·52, $Z=2$, $D_c=1\cdot18$,

$D_m = 1{\cdot}16$ g cm^{-3}. Space group $P\bar{1}$, $\lambda = 1{\cdot}54051$ Å, $\mu = 26{\cdot}26$ cm^{-1}.

A crystal of dimensions 0·36 × 0·20 × 0·02 mm was mounted along the *b* axis. The intensity data were collected on a Picker FACS-1 automatic diffractometer using the Vanderbilt disc-oriented program system of P. G. Lenhert. Reflexions up to $2\theta = 120°$ were recorded with graphite-monochromated Cu $K\alpha$ radiation in the θ–2θ mode with ten scan steps of 4 s each and a total scan width of 2°. 10s counts on both sides of the reflexions were taken to determine the background. 1966 reflexions were measured of which 1527 were greater than two standard deviations and included in the structure determination. Corrections were made for absorption and Lorentz–polarization but not for extinction.

Structure determination

The sulphur atoms were located from a sharpened Patterson series. A sulphur-phased electron density map revealed the positions of the remaining non-hydrogen atoms. With anisotropic temperature factors for the sulphur atoms, full-matrix least-squares refinement was performed. At an *R* value of 0·101 all hydrogen atoms except that of the carboxyl group were found from a difference Fourier series. The refinement was then continued with anisotropic temperature factors for the non-hydrogen atoms and fixed *B* values, corresponding to those of the parent atoms, for the hydrogens. When *R* had dropped to 0·084 the carboxyl hydrogen could be found from a difference map. This hydrogen was included in the calculation with a fixed *B* value and the refinement was continued until the average shift-over-error figure was 0·01. The *R* index was then 0·065.*

The weight assigned to each observation was $w = [1 + (F_o - 11)^2/12]^{-1}$. All atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) except for H, for which the data of Stewart, Davidson & Simpson (1965) were used.

Calculations were performed on a DEC 10 computer with the X-RAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Systems modifications for the DEC 10 were made by Dr Steve Ernst at Pittsburgh University and locally by one of us (R.P.).

Description of the structure

The final atomic parameters are given in Tables 1 and 2. Interatomic distances and angles are given in Fig. 1, which also gives standard deviations in bond lengths and shows the atomic numbering. Fig. 2 is a perspective view of the molecule and Fig. 3 shows the packing.

As in HES the ethyldithiocarbonate group is nearly planar (Table 3) with C(13) deviating 0·011 Å from the best plane. C(14) and C(15) are 0·022 and 0·109 Å respectively on opposite sides of the plane. As in HES also, the ω atom of the carboxylic acid [C(12)] is near the plane (0·017 Å).

The hydrocarbon chain deviates from the ideal zigzag conformation. Whereas the short chain of HES is planar within 0·005 Å the molecular packing in DOS causes distortions in the chain. The largest deviations from the best plane through C(2)–C(11) are

Table 1. *Fractional atomic coordinates*

The standard deviations (in parentheses) are multiplied by 10^5 for S, 10^3 for H and 10^4 for the other atoms.

	x	*y*	*z*	*B* (Å^2)
S(1)	−0·03442 (21)	−0·05910 (43)	0·66387 (7)	
S(2)	0·16865 (23)	0·10549 (45)	0·57055 (7)	
O(1)	1·7844 (6)	−0·3824 (11)	0·9827 (2)	
O(2)	1·9605 (6)	−0·7779 (11)	0·9561 (2)	
O(3)	−1·1679 (5)	0·2969 (10)	0·5991 (2)	
C(1)	1·8074 (8)	−0·6052 (15)	0·9581 (3)	
C(2)	1·6636 (9)	−0·7025 (15)	0·9252 (3)	
C(3)	1·5031 (8)	−0·4827 (14)	0·9117 (3)	
C(4)	1·3640 (8)	−0·6002 (15)	0·8784 (3)	
C(5)	1·2005 (8)	−0·3875 (15)	0·8620 (3)	
C(6)	1·0704 (8)	−0·5108 (14)	0·8270 (3)	
C(7)	0·9031 (8)	−0·3064 (15)	0·8102 (3)	
C(8)	0·7759 (8)	−0·4331 (15)	0·7748 (3)	
C(9)	0·6079 (8)	−0·2292 (14)	0·7581 (3)	
C(10)	0·4810 (8)	−0·3552 (15)	0·7225 (3)	
C(11)	0·3140 (8)	−0·1482 (15)	0·7068 (3)	
C(12)	0·1828 (9)	−0·2819 (16)	0·6739 (3)	
C(13)	−0·0089 (8)	0·1307 (13)	0·6074 (2)	
C(14)	−0·1915 (10)	0·4826 (18)	0·5531 (3)	
C(15)	−0·3749 (12)	0·6583 (23)	0·5589 (4)	
H(12)	2·024 (10)	−0·717 (14)	0·982 (3)	7·3
H(21)	1·720 (8)	−0·810 (13)	0·890 (3)	5·6
H(22)	1·619 (8)	−0·816 (13)	0·945 (2)	5·6
H(31)	1·448 (7)	−0·381 (12)	0·943 (2)	4·6
H(32)	1·541 (8)	−0·366 (13)	0·895 (2)	4·6
H(41)	1·422 (8)	−0·681 (12)	0·846 (2)	5·3
H(42)	1·332 (8)	−0·746 (13)	0·898 (2)	5·3
H(51)	1·144 (8)	0·315 (12)	0·895 (2)	4·9
H(52)	1·242 (8)	−0·234 (13)	0·845 (2)	4·9
H(61)	1·135 (8)	−0·598 (12)	0·796 (2)	5·2
H(62)	1·064 (8)	−0·689 (14)	0·836 (2)	5·2
H(71)	0·843 (8)	−0·245 (13)	0·837 (2)	5·1
H(72)	0·943 (8)	−0·167 (13)	0·794 (2)	5·1
H(81)	0·834 (7)	−0·496 (12)	0·742 (2)	4·9
H(82)	0·753 (8)	−0·569 (13)	0·795 (2)	4·9
H(91)	0·553 (7)	−0·138 (12)	0·790 (2)	4·9
H(92)	0·630 (8)	−0·069 (13)	0·746 (2)	4·9
H(101)	0·515 (8)	−0·417 (13)	0·695 (2)	4·9
H(102)	0·450 (7)	−0·529 (13)	0·742 (2)	4·9
H(111)	0·252 (8)	−0·075 (12)	0·739 (2)	5·0
H(112)	0·338 (8)	0·027 (13)	0·691 (2)	5·0
H(121)	0·219 (8)	−0·306 (13)	0·640 (2)	5·5
H(122)	0·161 (8)	−0·445 (13)	0·696 (2)	5·5
H(141)	−0·181 (9)	0·353 (14)	0·520 (3)	6·8
H(142)	−0·095 (9)	0·586 (14)	0·551 (2)	6·8
H(151)	−0·374 (10)	0·781 (16)	0·586 (3)	7·5
H(152)	−0·460 (10)	0·526 (15)	0·557 (3)	7·5
H(153)	−0·394 (9)	0·755 (15)	0·527 (3)	7·5

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* The structure-factor table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31615 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

found near the carboxylic group. This is forced into a chain matrix and its oxygen atoms are in contact with hydrogen atoms on C(2), C(4), C(5) and C(6). Similarly the ethyldithiocarbonate groups are surrounded by chains on two sides with close contact between S(1) and hydrogen atoms on C(7), C(8) and C(9).

The carboxyl group forms an angle of 17·6° with the carbon-chain plane. The corresponding angle in HES is 24·9°. The molecules are linked by hydrogen bonds to form dimers over centres of symmetry. The interplanar separation of bonded carboxyl groups is 0·234 Å. The hydroxyl hydrogen is in the plane of the symmetry-related carboxyl group.

The corresponding bond lengths of DOS and HES in the ethyldithiocarbonate agree remarkably well:

	DOS	HES
C(13)–S(2)	1·625 Å	1·617 Å
C(13)–S(1)	1·737	1·749
C(13)–O(3)	1·331	1·331
O(3)—C(14)	1·466	1·452
C(12)–S(1)	1·805	1·800
C(14)–C(15)	1·492	1·484
O(3)—C(13)–S(2)	126·6°	126·8°
S(2)—C(13)–S(1)	127·7	127·7
O(3)—C(13)–S(1)	105·7	105·5
C(13)–O(3)—C(14)	119·1	119·2
O(3)—C(14)–C(15)	105·2	106·5
C(13)–S(1)—C(12)	104·5	104·3

The mean C–C bond in the chain [C(2)–C(12)] is 1·508 Å (1·508) (the value within parentheses refers to HES) and the mean angle is 114·5° (113·5, this involves only four angles).

Table 2. *Anisotropic thermal parameters in the form exp* $[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2klb^*c^*U_{23}+2lha^*c^*U_{13}+2hka^*b^*U_{12})]$

Standard deviations are given in parentheses. All values have been multiplied by 10^4.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	410 (9)	930 (14)	387 (11)	136 (9)	−94 (7)	−83 (8)
S(2)	531 (11)	954 (15)	676 (12)	76 (10)	103 (8)	13 (9)
O(1)	499 (27)	757 (36)	971 (37)	−149 (31)	−266 (25)	−66 (24)
O(2)	568 (30)	880 (39)	869 (36)	−220 (29)	−324 (25)	−26 (27)
O(3)	401 (24)	855 (34)	594 (27)	130 (24)	−21 (19)	−1 (22)
C(1)	438 (37)	544 (42)	609 (41)	68 (34)	−133 (29)	−130 (32)
C(2)	511 (39)	567 (46)	725 (48)	−22 (36)	−236 (34)	−100 (33)
C(3)	437 (35)	557 (45)	540 (40)	−36 (32)	−121 (29)	−170 (31)
C(4)	433 (34)	592 (44)	605 (41)	−7 (34)	−171 (30)	−113 (31)
C(5)	410 (33)	637 (46)	561 (40)	3 (34)	−115 (28)	−184 (32)
C(6)	451 (35)	454 (39)	627 (41)	−79 (33)	−146 (30)	−39 (30)
C(7)	356 (32)	560 (43)	658 (44)	−15 (33)	−54 (29)	−52 (29)
C(8)	475 (35)	586 (44)	479 (36)	16 (32)	−90 (29)	−107 (31)
C(9)	469 (35)	498 (42)	564 (39)	−53 (33)	−65 (29)	−68 (31)
C(10)	402 (34)	615 (44)	538 (39)	−24 (33)	−104 (28)	−83 (31)
C(11)	437 (34)	559 (43)	569 (39)	−41 (34)	−34 (29)	−25 (31)
C(12)	513 (38)	703 (49)	555 (39)	48 (37)	−175 (32)	−52 (34)
C(13)	389 (32)	626 (43)	534 (36)	−106 (31)	−101 (27)	−95 (30)
C(14)	603 (44)	828 (58)	565 (42)	114 (40)	−44 (34)	43 (39)
C(15)	741 (56)	962 (80)	860 (64)	130 (52)	−155 (50)	120 (49)

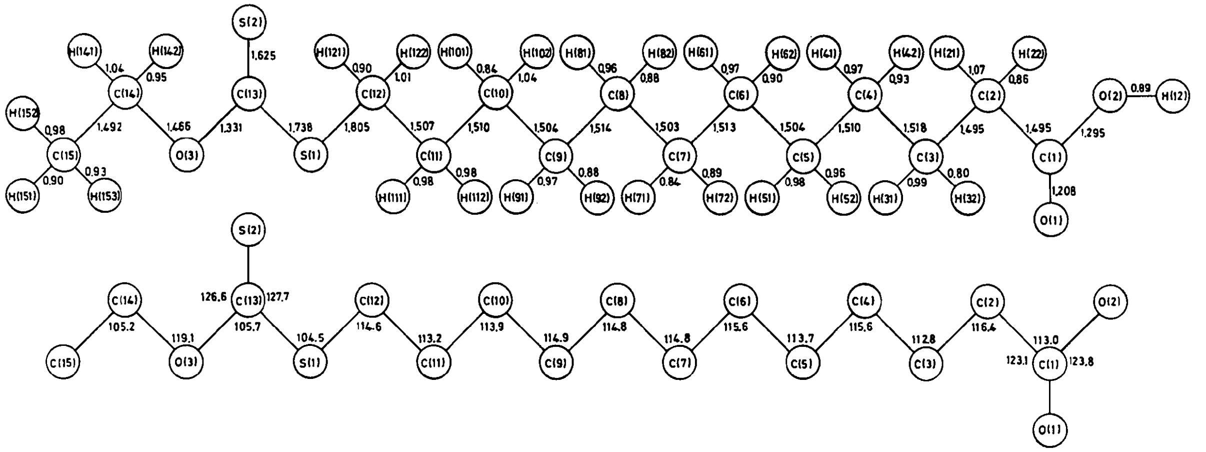

Fig. 1. Distances and angles of DOS. The standard deviations are for S–C bonds 0·006, for O–C bonds 0·008, for C–C bonds 0·010 and for C–H bonds 0·06 Å respectively.

Table 3. *Various least-squares planes through the molecule*

(Equations are referred to the crystal axes.)

Plane

I C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10), C(11)
$-4{\cdot}03394X-1{\cdot}63342Y+20{\cdot}66717Z-13{\cdot}59070=0$

II S(1), S(2), O(3), C(13)
$3{\cdot}27747X+3{\cdot}71666Y+13{\cdot}69680Z-8{\cdot}76365=0$

III O(1), O(2), C(1)
$-2{\cdot}55700X-2{\cdot}50946Y+20{\cdot}86903Z-16{\cdot}89285=0$

Distances from the various planes (Å)

	I	II	III
S(1)	0·365	−0·003*	−2·802
S(2)	−2·652	−0·004*	−5·682
O(1)	0·133	9·115	*
O(2)	−0·468	7·867	*
O(3)	−1·016	−0·004*	−4·705
C(1)	−0·091	8·034	*
C(2)	−0·033*	6·750	−0·076
C(3)	−0·024*	6·856	−0·499
C(4)	0·041*	5·506	−0·544
C(5)	0·014*	5·537	−1·002
C(6)	0·018*	4·174	−1·089
C(7)	0·011*	4·155	−1·526
C(8)	0·000*	2·782	−1·620
C(9)	−0·001*	2·761	−2·051
C(10)	−0·018*	1·389	−2·153
C(11)	−0·008*	1·395	−2·574
C(12)	0·059	0·017	−2·590
C(13)	−1·216	0·012*	−4·523
C(14)	−2·175	−0·022	−6·071
C(15)	−1·604	0·109	−5·924

* Atoms defining the planes.

The C–H bonds range from 0·80 to 1·07 Å with a mean value of 0·94 Å (0·95), the C–C–H angles from 100·4 to 114·6° with a mean value of 108·1° (108·8) and the H–C–H angles from 85·3 to 122·7° with a mean value of 107·3° (108·3).

The molecule is slightly bent at S(1). The angle between the chain axis and the tail of the ethyldithio-

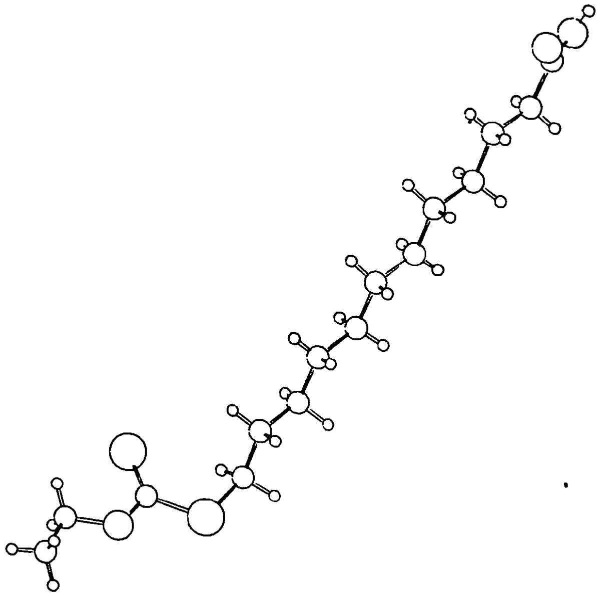

Fig. 2. Ball-and-stick drawing of DOS.

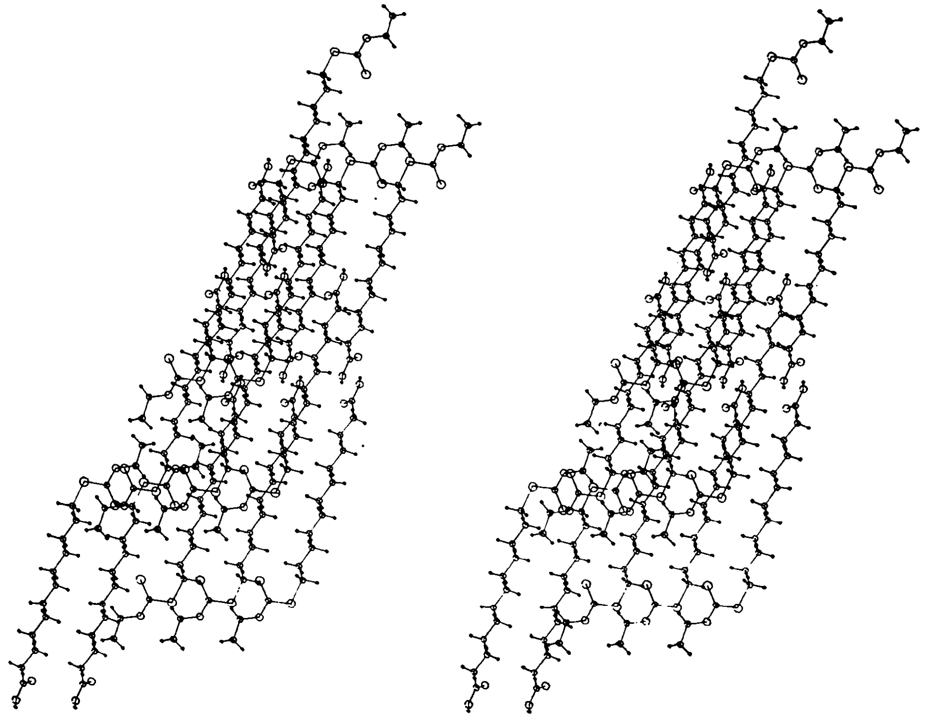

Fig. 3. Stereoscopic drawing of DOS.

carbonate group [C(13), O(3), C(4) and C(15)] is 143·8°. The corresponding angle in HES is 144·2°. The plane of the dithiocarbonate group is at an angle of 86·7° with the chain plane, compared to 83·6° in HES. As in HES, S(2) then comes into close intramolecular contact with one of the hydrogens on the ω-carbon atom in the chain, H(121), 2·63 Å, and the hydrogen atoms on C(14), 2·81 and 2·97 Å.

With this bend at S(1) the dithiocarbonate groups come into an interplanar contact of 3·72 Å. The bulkiness of these groups requires a relative translation along the chain axis so that the ethyl end of one molecule just reaches S(2) of a neighbouring one. This results in a very small region with carbon-chain lateral packing, which is described above. The chain arrangement can roughly be described by the subcell $a_s=4{\cdot}19$, $b_s=5{\cdot}85$, $c_s=2{\cdot}56$ Å, $\alpha_s=90$, $\beta_s=90$, $\gamma_s=126°$. In HES no such regions with chain packing could be formed. The triclinic subcell [with parallel zigzag planes ($T\|$)] has the following dimensions (Abrahamsson & Lundén, 1972): $a_s=4{\cdot}28$, $b_s=5{\cdot}37$, $c_s=2{\cdot}53$ Å, $\alpha_s=72{\cdot}3$, $\beta_s=108{\cdot}8$, $\gamma_s=117{\cdot}2°$.

A somewhat distorted monoclinic subcell ($M\|$) was recently found in 2-DL-hydroxytetradecanoic acid (Dahlén & Pascher, 1976) with $a_s=4{\cdot}74$, $b_s=4{\cdot}30$, $c_s=2{\cdot}54$ Å, $\alpha_s=94{\cdot}7$, $\beta_s=89{\cdot}2$, $\gamma_s=110{\cdot}9°$. As could be expected the chain arrangement in DOS does not agree with either $T\|$ or $M\|$.

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Conformation Moléculaire á l'Etat Solide de la *N*-Pivalyl-L-séryl-méthylamide

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The structure of *N*-pivalyl-L-seryl-methylamide has been determined from three-dimensional X-ray diffractometer data. This compound crystallizes in the monoclinic system with cell constants: $a=9{\cdot}66$, $b=6{\cdot}59$, $c=17{\cdot}72$ Å, $\beta=94{\cdot}03°$, space group $A2$. The structure was solved by a direct method of phase determination and was refined by least-squares methods. The final reliability index is 0·044. The conformational angles φ, ψ and χ_1 are -88, 151 and 70° respectively.

Introduction

Poursuivant l'étude sur les conformations à l'état solide de peptides condensés possédant des extrémités de chaîne substituées par des groupements inertes, nous avons déterminé la structure cristalline de la *N*-pivalyl-L-séryl-méthylamide. A notre connaissance, aucune structure cristalline d'oligopeptide linéaire contenant le résidu séryl n'a été résolue à ce jour. Seules sont connues les conformations de la sérine (Frey, Lehmann, Koetzle & Hamilton, 1973), DL-sérine (Kistenmacher, Rand & Marsh, 1974), L-sérine monohydratée (Benedetti, Pedone & Sirigu, 1972), de plusieurs complexes réalisés avec le zinc (van der Helm, Nicholas & Fisher,