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3-Chloro-4-dimethylaminothioangelicin

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Abstract. $C_{13}H_{10}ClO_2NS$, $M_r = 279{\cdot}75$, monoclinic, $P2_1/a$, $a = 14{\cdot}490$ (3), $b = 22{\cdot}598$ (5), $c = 7{\cdot}336$ (2) Å, $\beta = 92{\cdot}4$ (1)°, $U = 2400$ (1) Å^3, $Z = 8$, $D_x = 1{\cdot}548$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}07$ cm^{-1}, $F(000) = 1152$, room temperature, $R = 0{\cdot}037$ for 2423 independent reflections with $I \geq 3\sigma(I)$. Each unit cell contains two independent molecules which differ mainly in the orientation of their $N(CH_3)_2$ groups. The two tricyclic moieties of each molecule are not coplanar, the pyran ring being tilted by 7·9 (1)° with respect to the benzene ring in molecule 1 and by 8·7 (1)° in molecule 2. There are weak interactions between the molecules involving the carboxylic O atoms and the H atoms of the phenyl moieties.

Introduction. Methyl angelicins such as 4,6,4′-trimethylangelicin have recently been proposed as alternative drugs to psoralens in the photochemotherapeutic treatment of psoriasis (Guiotto, Rodighiero, Manzini, Pastorini, Bordin, Baccichetti, Carlassare, Vedaldi, Dall'Acqua, Tanaro, Recchia & Cristofolini, 1984).

More recently other angelicin derivatives functionalized in the 3- and 4-positions, *i.e.* 3-chloro-4-(*N*,*N*-dialkylamino)angelicins, have been prepared and studied. Some of them show marked antiproliferative activity under UV-*A* irradiation (Mosti, Schenone, Menozzi, Romussi, Baccichetti, Carlassare, Vedaldi & Bordin, 1983). The interactions between some of these compounds and DNA have been studied (Vedaldi, Dall'Acqua, Baccichetti, Bombieri, Schenone & Mosti, 1986) and the role of the functional groups in terms of influence on the complex with DNA in the ground state and on DNA photobinding (Benetollo, Bombieri, Mosti, Vedaldi & Dall'Acqua, 1984) has also been investigated.

Recently bioisosters of 3-amino-4-(*N*,*N*-dialkylamino)angelicins have been prepared by replacing the O atom of the furan ring with an S atom (Mosti, Schenone, Menozzi, Romussi, Baccichetti, Carlassare & Bordin, 1983). Among them 3-chloro-4-dimethylaminothioangelicin appeared a good candidate for evaluating how the structural parameters can affect the interactions of this compound with DNA. Its crystal and molecular structure was then determined.

Experimental. Crystals obtained from ethanol; crystal dimensions 0·18 × 0·20 × 0·32 mm; PW 1100 diffractometer with monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å); 25 reflections $8 < \theta < 12°$ used for refinement of cell dimensions; index ranges h −17 to 17, k 0 to 26, l 0 to 8; two reflections (222 and 260) measured every 180 min of X-ray exposure time. Scan width 1·20°, scan speed 0·03° s^{-1}, total background measuring time 20 s; 2θ range 4–50°; total number of reflections measured 4697, 2423 reflections with $I \geq 3\sigma(I)$ used in the analysis; corrections for Lorentz and polarization effects, but not for absorption. Structure solved by direct methods (Hull, Viterbo, Woolfson & Shao-Hui, 1981) and refined by a full-matrix least-squares procedure, with anisotropic thermal parameters for all non-H atoms; $\sum w(\Delta F)^2$ minimized, $R = 0{\cdot}037$, $wR = 0{\cdot}035$, $w = 2{\cdot}39034[\sigma(F_o) + 0{\cdot}000186(F_o)]^{-1}$; H atoms located by difference Fourier maps, refined with isotropic temperature factors; $S = 1{\cdot}19$, $(\Delta/\sigma)_{max} = 0{\cdot}06$, maximum $\Delta\rho$ excursions 0·18 and −0·20 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974);

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Table 1. *Atomic coordinates* ($\times 10^4$) *and* U_{eq} *values* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Molecule 1				
Cl(1)	2546·3 (6)	206·1 (4)	2709·2 (1·3)	63·4 (3)
S(11)	3944·8 (7)	3741·2 (4)	4557·5 (1·5)	71·5 (4)
N(1)	4496 (2)	794 (1)	3068 (4)	52 (1)
O(1)	2213 (1)	1883 (1)	3915 (3)	49·4 (8)
O(2)	1245 (2)	1152 (1)	3363 (3)	65 (1)
C(2)	2045 (2)	1305 (1)	3391 (4)	50 (1)
C(3)	2835 (2)	944 (1)	3043 (4)	45 (1)
C(4)	3728 (2)	1142 (1)	3215 (4)	43 (1)
C(5)	4690 (2)	2080 (2)	3302 (5)	54 (2)
C(6)	4779 (3)	2674 (2)	3598 (5)	61 (2)
C(7)	4010 (2)	2989 (1)	4111 (4)	52 (1)
C(8)	3149 (2)	2724 (1)	4257 (4)	47 (1)
C(9)	3086 (2)	2116 (1)	3909 (4)	42 (1)
C(10)	3849 (2)	1778 (1)	3525 (4)	44 (1)
C(12)	2789 (3)	3688 (2)	4896 (5)	68 (2)
C(13)	2449 (2)	3140 (2)	4706 (5)	53 (1)
C(14)	5303 (3)	859 (2)	4292 (6)	62 (2)
C(15)	4571 (3)	323 (2)	1751 (6)	61 (2)
Molecule 2				
Cl(11)	2848·3 (6)	204·5 (4)	7664·4 (1·3)	59·9 (3)
S(111)	1514·4 (6)	3742·5 (4)	9510·2 (1·4)	63·1 (4)
N(11)	898 (2)	805 (1)	8051 (4)	47·8 (9)
O(11)	3227 (1)	1886 (1)	8787 (3)	47·0 (8)
O(21)	4165 (2)	1164 (1)	8088 (3)	64 (1)
C(21)	3373 (2)	1309 (1)	8224 (4)	46 (1)
C(31)	2565 (2)	945 (1)	7968 (4)	42 (1)
C(41)	1681 (2)	1143 (1)	8157 (4)	40 (1)
C(51)	720 (2)	2077 (1)	8267 (5)	50 (1)
C(61)	644 (2)	2670 (2)	8555 (5)	53 (1)
C(71)	1433 (2)	2989 (1)	9072 (4)	46 (1)
C(81)	2303 (2)	2727 (1)	9204 (4)	43 (1)
C(91)	2357 (2)	2118 (1)	8835 (4)	39 (1)
C(101)	1575 (2)	1781 (1)	8467 (4)	40 (1)
C(121)	2688 (3)	3686 (2)	9880 (5)	60 (2)
C(131)	3027 (2)	3138 (2)	9674 (5)	50 (1)
C(141)	225 (3)	848 (2)	9457 (6)	65 (2)
C(151)	793 (3)	278 (2)	6927 (6)	60 (1)

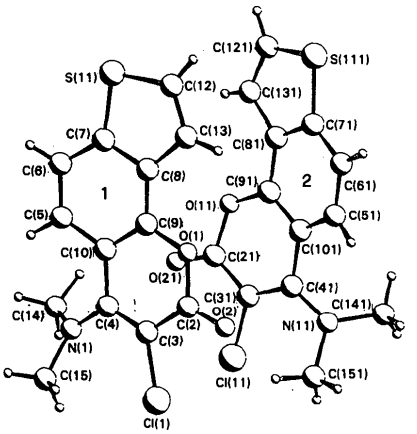

Fig. 1. Perspective view of the asymmetric units.

all calculations performed on a VAX 11/750 computer with the *SHELX76* (Sheldrick, 1976) program package. All geometrical calculations performed with *PARST* (Nardelli, 1983) and drawings with *PLUTO* (Motherwell & Clegg, 1978).

The formation of the dark complex between the title compound and calf thymus DNA (Sigma Chemical Company, St Louis, USA, D1501) was studied by fluorescence quenching of the ligand using a Perkin Elmer spectrophotofluorimeter, model L55.

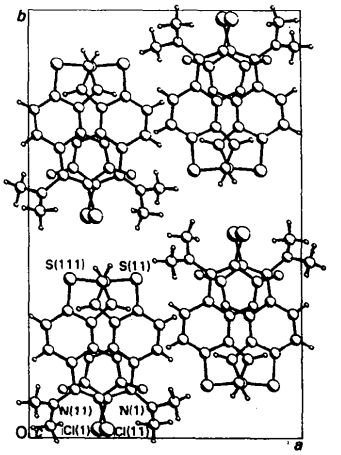

Fig. 2. Cell content as viewed down **c**.

The quantitative binding of the ligand to the DNA was followed by means of fluorimetric titration (Vedaldi, Rodighiero, Guiotto, Bordin, Caffieri & Dall'Acqua, 1981) determining the values of r (molecules of ligand bound per nucleotide) and c (molecules of ligand free in the system). From these experimental values the binding parameters of the complex, *i.e.* K (association constant related to an isolated site) = 7070 and n (number of nucleotides occluded by a bound ligand) = 12·74 have been determined (McGhee & von Hippel, 1974).

Discussion. Atomic coordinates and equivalent isotropic temperature factors are given in Table 1.*

The structure consists of two independent molecules which are shown in Fig. 1 together with their atom-numbering scheme (equivalent atoms in the second molecule are indicated by adding 1 to the corresponding atom of molecule 1). A packing diagram is shown in Fig. 2.

Bond distances and angles in the two molecules (Table 2) are in good agreement and are comparable with the analogous values in the parent compound, 3-chloro-4-dimethylaminoangelicin (hereafter *B*) (Benetollo, Bombieri, Mosti, Vedaldi & Dall'Acqua, 1984). Mean-plane calculations through the tricyclic moiety in the two molecules show a higher degree of planarity in molecule 1. The Δ values range from −0·080 (3) to 0·137 (3) Å for molecule 1 and from

* Lists of structure factors, anisotropic thermal parameters, weighted least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44953 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Molecule 1		Molecule 2	
Cl(1)–C(3)	1·734 (3)	Cl(11)–C(31)	1·740 (3)
S(11)–C(7)	1·734 (3)	S(111)–C(71)	1·736 (3)
S(11)–C(12)	1·708 (4)	S(111)–C(121)	1·716 (4)
N(1)–C(4)	1·371 (4)	N(11)–C(41)	1·367 (4)
N(1)–C(14)	1·452 (5)	N(11)–C(141)	1·452 (6)
N(1)–C(15)	1·445 (5)	N(11)–C(151)	1·453 (5)
O(1)–C(2)	1·380 (3)	O(11)–C(21)	1·387 (3)
O(1)–C(9)	1·370 (3)	O(11)–C(91)	1·367 (3)
O(2)–C(2)	1·209 (4)	O(21)–C(21)	1·202 (4)
C(2)–C(3)	1·437 (4)	C(21)–C(31)	1·437 (4)
C(3)–C(4)	1·370 (4)	C(31)–C(41)	1·369 (4)
C(4)–C(10)	1·464 (3)	C(41)–C(101)	1·469 (3)
C(5)–C(6)	1·365 (6)	C(51)–C(61)	1·362 (5)
C(5)–C(10)	1·412 (4)	C(51)–C(101)	1·410 (4)
C(6)–C(7)	1·387 (5)	C(61)–C(71)	1·391 (4)
C(7)–C(8)	1·392 (4)	C(71)–C(81)	1·392 (4)
C(8)–C(9)	1·400 (3)	C(81)–C(91)	1·405 (3)
C(8)–C(13)	1·431 (5)	C(81)–C(131)	1·432 (5)
C(9)–C(10)	1·382 (4)	C(91)–C(101)	1·382 (4)
C(12)–C(13)	1·338 (6)	C(121)–C(131)	1·343 (6)
C(7)–S(11)–C(12)	91·1 (2)	C(71)–S(111)–C(121)	90·9 (2)
C(14)–N(1)–C(15)	114·0 (4)	C(151)–N(11)–C(141)	113·6 (4)
C(4)–N(1)–C(15)	124·0 (4)	C(41)–N(11)–C(151)	123·9 (4)
C(4)–N(1)–C(14)	121·9 (3)	C(41)–N(11)–C(141)	120·2 (3)
C(2)–O(1)–C(9)	121·0 (3)	C(21)–O(10)–C(91)	121·4 (3)
O(1)–C(2)–O(2)	115·7 (3)	O(11)–C(21)–O(21)	116·1 (4)
O(2)–C(2)–C(3)	127·2 (2)	O(21)–C(21)–C(31)	127·5 (2)
O(1)–C(2)–C(3)	117·0 (3)	O(11)–C(21)–C(31)	116·3 (3)
Cl(1)–C(3)–C(2)	112·4 (2)	Cl(11)–C(31)–C(21)	111·8 (2)
C(2)–C(3)–C(4)	123·7 (2)	C(21)–C(31)–C(41)	124·1 (2)
Cl(1)–C(3)–C(4)	123·3 (2)	Cl(11)–C(31)–C(41)	123·6 (2)
N(1)–C(4)–C(3)	124·9 (2)	N(11)–C(41)–C(31)	126·1 (2)
C(3)–C(4)–C(10)	116·2 (3)	C(31)–C(41)–C(101)	116·2 (3)
N(1)–C(4)–C(10)	118·9 (4)	N(11)–C(41)–C(101)	117·7 (3)
C(6)–C(5)–C(10)	122·2 (4)	C(61)–C(51)–C(101)	121·8 (3)
C(5)–C(6)–C(7)	118·4 (4)	C(51)–C(61)–C(71)	118·8 (4)
S(11)–C(7)–C(6)	127·2 (3)	S(111)–C(71)–C(61)	127·4 (3)
C(6)–C(7)–C(8)	122·2 (3)	C(61)–C(71)–C(81)	122·0 (3)
S(11)–C(7)–C(8)	110·6 (2)	S(111)–C(71)–C(81)	110·5 (2)
C(7)–C(8)–C(13)	112·4 (3)	C(71)–C(81)–C(131)	113·1 (3)
C(7)–C(8)–C(9)	117·4 (3)	C(71)–C(81)–C(91)	117·4 (3)
C(9)–C(8)–C(13)	130·2 (3)	C(91)–C(81)–C(131)	129·4 (3)
O(1)–C(9)–C(8)	115·4 (3)	O(11)–C(91)–C(81)	116·1 (3)
C(8)–C(9)–C(10)	122·2 (3)	C(81)–C(91)–C(101)	121·7 (3)
O(1)–C(9)–C(10)	122·3 (2)	O(11)–C(91)–C(101)	122·2 (2)
C(5)–C(10)–C(9)	117·3 (3)	C(51)–C(101)–C(91)	117·9 (2)
C(4)–C(10)–C(9)	118·8 (3)	C(41)–C(101)–C(91)	118·7 (3)
C(4)–C(10)–C(5)	123·7 (3)	C(41)–C(101)–C(51)	123·1 (3)
S(11)–C(12)–C(13)	114·2 (4)	S(111)–C(121)–C(131)	114·6 (4)
C(8)–C(13)–C(12)	111·7 (4)	C(81)–C(131)–C(121)	110·9 (4)

−0·128 (3) to 0·173 (3) Å for molecule 2. The two tricyclic moieties are inclined at 13·6 (1)°. Least-squares mean-planes data show that the three rings of each molecule are not coplanar: the pyran ring forms an angle of 7·9 (1)° (in molecule 1) and 8·7 (1)° (in molecule 2) with the central benzene ring, while the benzene and the thiophene moieties are practically coplanar in both molecules. The methyl groups are, in order to reduce steric hindrance, arranged in asymmetric fashion with respect to the adjacent pyran rings [from which the deviations of the respective $N(CH_3)_2$ groups are: N(1) −0·213 (3), C(15) 0·462 (4), C(14) −1·115 (4), N(11) −0·204 (3), C(151) 0·309 (4) and C(141) −1·214 (4) Å]. In particular the substitution of the O atom by an S atom in the furan ring causes significant changes in the bond angles, whereas apart from the obviously different S–C and O–C distances, the bond lengths are exactly comparable.

The two S–C bond distances are non-equivalent: those adjacent to the central rings are longer with respect to the others [S(11)–C(7) = 1·734 (3) *vs* S(11)–C(12) = 1·708 (4) Å and S(111)–C(71) = 1·736 (3) *vs* S(111)–C(121) 1·716 (4) Å], although the C–S–C angles have the expected values. This fact has also been noticed in 1-methylphenanthro[3,4-*b*]-thiophene (Musmar, Martin, Gampe, Lynch, Symonsen, Lee, Tedjamulia & Castle, 1985) and can be attributed to strains in the condensed ring system where, because of the lack of coplanarity, electron delocalization seems to be absent.

The non-isostructurality of the two compounds is due to their different packing modes; in *B* adjacent centrosymmetrically related molecules have their furan moieties partially superimposed with short contacts between them, while the terminal phenyl group of molecule 1 is partially superimposed on the terminal phenyl group of molecule 2 (also in this case two molecules constitute the asymmetric units). Here the two closest molecules (1 and 2) are partially superimposed side by side (see Fig. 1) with the more hindered part of the molecule, the $N(CH_3)_2$ groups, lying on the external sides. (The two molecules are related by a pseudo-binary axis in the direction of the *b* axis.) The carboxylic O(2) atom in molecule 1 and O(21) in molecule 2 are involved in weak interactions with the H atoms of molecules of the same type {C(6)···O(2^{i}) [(i) $\frac{1}{2}+x$, $\frac{1}{2}-y$, z] 3·408 (5), C(6)–H(8)···O(2^{i}) 2·62 (3) Å and an angle of 145 (3)°, while C(61)···O(21^{ii}) [(ii) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, z] is 3·405 (5) Å, C(61)–H(81)···O(21^{ii}) 2·60 (3) Å and the angle is 150 (3)°}. These interactions cause the formation of parallel chains (one involving molecules 1 the second involving molecules 2)

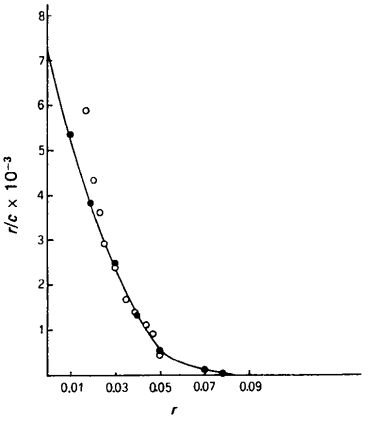

Fig. 3. Scathchard plot of the binding of 3-chloro-4-dimethylaminothioangelicin to DNA obtained by plotting r/c against r, where r represents the molecules of ligand bound per nucleotide and c the molecules of ligand free in the system (mol l^{-1}). The curves have been computed according to the method of McGhee & von Hippel (1974). $K(M^{-1})$ is obtained from the intercept of the curve with the ordinate, while n is obtained from the intercept of the curve with the abscissa.

in the direction of the crystallographic axis, with a Cl(1)···Cl(11) separation of 3·643 (2) Å.

The molecular thickness is 3·05 Å in 1 and 3·30 Å in 2, *i.e.* close to that of *B*, making a partial intercalation inside duplex DNA possible in principle as in *B*. In this connection 3-chloro-4-dimethylaminothioangelicin shows an evident affinity towards DNA in the dark, forming a molecular complex with the macromolecule as shown by the classic Scathchard plot reported in Fig. 3. In fact, the *K* value ($7070\ M^{-1}$) correlated to the affinity of the ligand towards DNA is much higher than that of the parent compound angelicin ($K = 560\ M^{-1}$) (Dall'Acqua, Vedaldi, Guiotto, Rodighiero, Carlassare, Baccichetti & Bordin, 1981).

The substitution of oxygen in *B* by sulfur, in addition to the crystal-packing changes, seems to affect the electronic arrangement of the chromophore at the excited state probably reducing the DNA photobinding. In fact the antiproliferative activity, which is correlated with the DNA photobinding, is poor (Mosti, Schenone, Menozzi, Romussi, Baccichetti, Carlassare & Bordin, 1983).

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Echinatine, $C_{15}H_{25}NO_5$, a Pyrrolizidine Alkaloid

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Abstract. $M_r = 299{\cdot}4$, monoclinic, $P2_1$, $a = 7{\cdot}214$ (1), $b = 13{\cdot}577$ (1), $c = 9{\cdot}005$ (1) Å, $\beta = 111{\cdot}58$ (1)°, $V = 820{\cdot}2$ (1) Å^3, $Z = 2$, D_m (flotation) = 1·21 (1), $D_x = 1{\cdot}213$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}66$ mm^{-1}, $F(000) = 324$, $T = 288$ (1) K, final $R = 0{\cdot}052$ for 1364 observed reflections. Echinatine, a heliotridine alkaloid, is a diastereoisomer of lycopsamine, a retronecine ester with the same esterifying acid. The pyrrolizidine nucleus in echinatine is *exo*-puckered in contrast to the *endo*-puckering in crystals of two other heliotridine alkaloids, heliotrine and lasiocarpine. As observed in the other monoester alkaloids the esterifying acid moiety, in this case (−)-viridifloric acid, adopts an extended conformation. Hydrogen bonding in the crystal links the molecules into layers parallel to the *bc* plane.

Introduction. Echinatine (I), a monoester of the aminoalcohol heliotridine with (−)-viridifloric acid, is a pyrrolizidine alkaloid which has been isolated from

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