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Structure of Tetrahydroaplysulphurin-1

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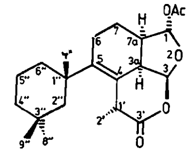
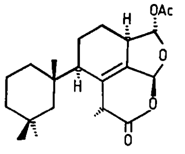
Abstract. 2-(Acetyloxy)-2a,3,4,6,8a,8b-hexahydro-6-methyl-5-(1,3,3-trimethylcyclohexyl)furo[4,3,2-*ij*][2]-benzopyran-7(2*H*)-one, $C_{22}H_{32}O_5$, $M_r = 376{\cdot}66$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}637\ (2)$, $b = 14{\cdot}127\ (1)$, $c = 15{\cdot}141\ (2)$ Å, $V = 2061{\cdot}4$ Å^3, $T = 292$ K, $D_x = 1{\cdot}21$ g cm^{-3}, $Z = 4$, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}5418$ Å, Ni filter, $\mu = 0{\cdot}90$ cm^{-1}, $F(000) = 816$, $R = 0{\cdot}053$ for 567 $[I > 2{\cdot}5\sigma(I)]$ reflections. The X-ray study confirms the previously proposed structure of tetrahydroaplysulphurin-1. There are no unusual bond lengths or angles.

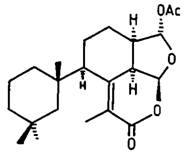
Introduction. Recently, Karuso, Bergquist, Cambie, Buckleton, Clark & Rickard (1986) reported the isolation and structural determination of a new diterpenoid, tetrahydroaplysulphurin-1 (1), from the sponge *Darwinella* sp. Compound (1) was also obtained from *Darwinella oxeata* along with its isomers tetrahydroaplysulphurin-2 (2) and tetrahydroaplysulphurin-3 (3). Although little doubt existed as to their structures the stereochemistry at C(1′), C(1″), C(3) and C(1) of (1) was assigned by analogy with that of aplysulphurin (4) of known structure (Karuso, Skelton, Taylor & White, 1984), while that of the two new chiral centres C(3a) and C(7a) was assigned from biogenetic considerations and ^{1}H NMR coupling constants. We now report a single-crystal X-ray determination which confirms the structure of tetrahydroaplysulphurin-1 as (1).



(1)



(2)



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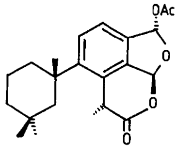

(4)

Experimental. Crystals were obtained as colourless needles. A fragment $0{\cdot}50 \times 0{\cdot}16 \times 0{\cdot}16$ mm was mounted on a Nonius CAD-4 diffractometer; Ni-filtered Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å; unit-cell dimensions from 25 reflections, $16{\cdot}8 < \theta < 25{\cdot}0°$; systematic absences $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$ defined space group as $P2_12_12_1$; 1320 unique reflections, $0 < 2\theta < 120°$, $[(\sin\theta)/\lambda]_{\text{max}}\ 0{\cdot}5617$ Å^{-1}; 567 with $I > 2{\cdot}5\sigma(I)$, $0 \leq h \leq 9$, $0 \leq k \leq 12$, $0 \leq l \leq 16$; three intensity standards checked every hour showed no non-statistical variation during X-ray exposure; absorption corrections were applied using azimuthal scan data, maximum and minimum correction factors 0·9993 and 0·9537 respectively. Data were processed using the Enraf–Nonius (1981) *Structure Determination Package* on a PDP-11 computer. Structure solved using *SHELXS*86 (Sheldrick, 1986), and refined using *SHELX*76 (Sheldrick, 1976) on the University of Auckland IBM 4341 computer. The function minimized was $\sum w(|F_o| - |F_c|)^2$. H atoms were placed in geometrically derived positions (C—H 1·0 Å) and allowed to ride on the C atoms during refinement. O atoms were assigned anisotropic thermal parameters. Reflection weights in the final cycle of refinement were $w = 1{\cdot}2941/[\sigma^2(F) + gF^2]$ with g being $1{\cdot}269 \times 10^{-3}$, $S = 1{\cdot}44$. Final R and wR were 0·053 and 0·054 respectively, $(\Delta/\sigma)_{\text{max}} = 0{\cdot}33$ for positions; max. $\Delta\rho$ excursion in final difference map 0·17 e Å^{-3}. Diagrams were produced using *ORTEP* (Johnson, 1965). Atomic scattering factors those of *SHELX*.

Discussion. The compound is monomeric. Atomic positions are listed in Table 1.§ The molecular geometry and atomic numbering are shown in Fig. 1, which does not necessarily depict the true chirality of the molecule. The unit-cell packing is given in the stereopair diagram of Fig. 2.

The X-ray analysis confirms the structure of tetrahydroaplysulphurin-1 as (1), and establishes the relative

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§ Lists of anisotropic thermal parameters, H-atom positions and observed and calculated structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44306 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters* (× 10^4) *and isotropic thermal parameters for tetrahydroaplysulphurin*-1

	x	y	z	U(Å^2 × 10)
O(1)	653 (9)	3725 (6)	9492 (5)	45 (4)*
O(1′)	439 (9)	2519 (8)	8548 (6)	47 (4)*
O(2)	1819 (13)	2747 (9)	403 (5)	93 (6)*
O(3)	2241 (9)	1968 (6)	1657 (5)	46 (4)*
O(3′)	2507 (11)	1104 (7)	2841 (6)	62 (5)*
C(1)	487 (16)	3101 (11)	214 (9)	64 (5)
C(1′)	1899 (12)	2715 (8)	3088 (7)	38 (4)
C(1″)	−1043 (14)	3044 (9)	3885 (7)	47 (4)
C(1)	601 (15)	3326 (11)	8687 (10)	51 (5)
C(2′)	3196 (14)	3331 (10)	3199 (9)	67 (5)
C(2″)	−165 (14)	3559 (8)	4607 (8)	53 (4)
C(2)	846 (17)	4063 (11)	7987 (9)	85 (5)
C(3)	2196 (16)	2893 (10)	1270 (9)	57 (4)
C(3a)	1111 (13)	3533 (9)	1713 (7)	41 (4)
C(3′)	2266 (15)	1876 (11)	2526 (9)	50 (4)
C(3″)	−405 (14)	4615 (10)	4722 (9)	55 (4)
C(4)	704 (12)	3200 (9)	2617 (7)	41 (4)
C(4″)	−1923 (14)	4833 (10)	4866 (9)	79 (5)
C(5)	−594 (12)	3301 (8)	2941 (8)	36 (3)
C(5″)	−2830 (15)	4374 (9)	4159 (8)	65 (5)
C(6)	−1690 (14)	3608 (10)	2268 (7)	58 (4)
C(6″)	−2556 (14)	3342 (9)	4099 (9)	68 (5)
C(7)	−1414 (13)	3216 (9)	1357 (8)	55 (4)
C(7a)	−71 (13)	3628 (10)	1020 (8)	46 (4)
C(7″)	−988 (16)	1971 (9)	3998 (9)	64 (4)
C(8″)	206 (16)	5190 (10)	3966 (9)	62 (5)
C(9″)	470 (17)	4902 (11)	5551 (10)	87 (6)

* Equivalent isotropic thermal parameter:
$U_{\rm eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

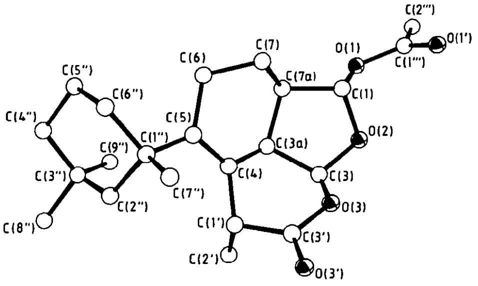

Fig. 1. The molecular geometry and atomic numbering for tetrahydroaplysulphurin-1. Oxygen atoms are represented as 50% probability ellipses.

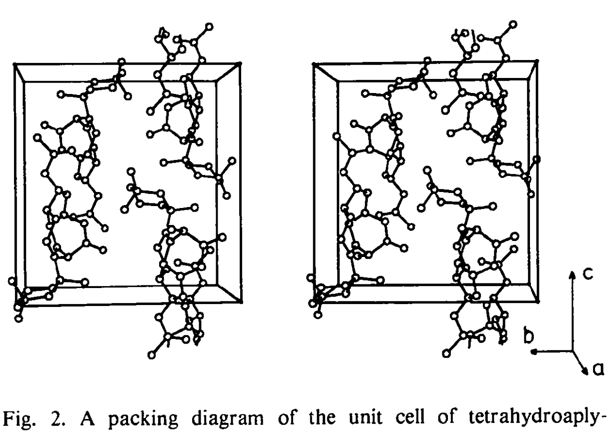

Fig. 2. A packing diagram of the unit cell of tetrahydroaplysulphurin-1.

Table 2. *Bond lengths* (Å) *and angles* (°) *for tetrahydroaplysulphurin*-1

O(1)–C(1)	1·414 (15)	C(1″)–C(7″)	1·526 (15)
O(1)–C(1‴)	1·343 (15)	C(1‴)–C(2‴)	1·505 (16)
O(1′)–C(1‴)	1·169 (13)	C(2″)–C(3″)	1·520 (16)
O(2)–C(1)	1·407 (15)	C(3)–C(3a)	1·537 (17)
O(2)–C(3)	1·377 (15)	C(3a)–C(4)	1·498 (14)
O(3)–C(3)	1·434 (14)	C(3a)–C(7a)	1·555 (16)
O(3)–C(3′)	1·322 (13)	C(3″)–C(4″)	1·511 (17)
O(3′)–C(3′)	1·213 (15)	C(3″)–C(8″)	1·522 (16)
C(1)–C(7a)	1·527 (17)	C(3″)–C(9″)	1·566 (17)
C(1′)–C(2′)	1·532 (16)	C(4)–C(5)	1·352 (14)
C(1′)–C(3′)	1·501 (16)	C(4″)–C(5″)	1·527 (16)
C(1′)–C(4)	1·518 (15)	C(5)–C(6)	1·530 (15)
C(1″)–C(2″)	1·562 (16)	C(5″)–C(6″)	1·484 (15)
C(1″)–C(5)	1·537 (15)	C(6)–C(7)	1·510 (14)
C(1″)–C(6″)	1·552 (18)	C(7)–C(7a)	1·508 (18)

C(1)–O(1)–C(1‴)	115·8 (10)	C(4)–C(3a)–C(7a)	116·8 (11)
C(1)–O(2)–C(3)	112·4 (11)	O(3)–C(3′)–O(3′)	118·8 (14)
C(3)–O(3)–C(3′)	119·8 (11)	O(3)–C(3′)–C(1′)	118·9 (13)
O(1)–C(1)–O(2)	106·0 (12)	O(3′)–C(3′)–C(1′)	122·2 (11)
O(1)–C(1)–C(7a)	110·7 (11)	C(2″)–C(3″)–C(4″)	111·4 (12)
O(2)–C(1)–C(7a)	109·4 (12)	C(2″)–C(3″)–C(8″)	112·3 (12)
C(2′)–C(1′)–C(3′)	108·5 (10)	C(2″)–C(3″)–C(9″)	105·3 (12)
C(2′)–C(1′)–C(4)	114·4 (10)	C(4″)–C(3″)–C(8″)	112·0 (12)
C(3′)–C(1′)–C(4)	105·6 (10)	C(4″)–C(3″)–C(9″)	110·7 (12)
C(2″)–C(1″)–C(5)	112·9 (10)	C(8″)–C(3″)–C(9″)	104·8 (10)
C(2″)–C(1″)–C(6″)	103·7 (10)	C(1′)–C(4)–C(3a)	111·9 (10)
C(2″)–C(1″)–C(7″)	111·4 (11)	C(1′)–C(4)–C(5)	125·3 (11)
C(5)–C(1″)–C(6″)	113·3 (11)	C(3a)–C(4)–C(5)	122·8 (12)
C(5)–C(1″)–C(7″)	109·2 (10)	C(3″)–C(4″)–C(5″)	111·5 (12)
C(6″)–C(1″)–C(7″)	106·1 (12)	C(1″)–C(5)–C(4)	125·0 (11)
O(1)–C(1‴)–O(1′)	125·3 (14)	C(1″)–C(5)–C(6)	119·5 (10)
O(1)–C(1‴)–C(2‴)	110·1 (12)	C(4)–C(5)–C(6)	115·2 (11)
O(1′)–C(1‴)–C(2‴)	124·6 (15)	C(4″)–C(5″)–C(6″)	111·1 (13)
C(1″)–C(2″)–C(3″)	117·0 (11)	C(5)–C(6)–C(7)	112·5 (11)
O(2)–C(3)–O(3)	105·2 (11)	C(1″)–C(6″)–C(5″)	116·5 (13)
O(2)–C(3)–C(3a)	108·9 (12)	C(6)–C(7)–C(7a)	108·6 (11)
O(3)–C(3)–C(3a)	112·2 (11)	C(1)–C(7a)–C(3a)	103·8 (10)
C(3)–C(3a)–C(4)	113·1 (11)	C(1)–C(7a)–C(7)	112·6 (11)
C(3)–C(3a)–C(7a)	104·8 (10)	C(3a)–C(7a)–C(7)	111·5 (10)

stereochemistries at the chiral centres. Bond distances and angles are listed in Table 2. All values are normal. The bond O(1′)—C(1‴) appears a little short at 1·169 (13) Å, but it is in fact less than 3σ from an acceptable distance of 1·20 Å. The bond length O(3)—C(3′) of 1·322 (13) Å is 0·06 Å shorter than the O(2)—C(1) and O(2)—C(3) bonds (the difference in covalent radii between sp^2- and sp^3-hybridized carbon). There are no significantly short intermolecular interactions.

The structure can be compared with that of aplysulphurin (4) (Karuso, Skelton, Taylor & White, 1984). Loss of the aromatic ring of (4) by four-hydrogen reduction obviously causes that ring in (1) to become non-planar, and it adopts a twisted-boat arrangement. The relative stereochemistries at the new chiral centres C(3a) and C(7a) are as shown in Fig. 1. The five-membered ring which was an envelope in (4) with the cyclic oxygen deviant from the plane of the other four atoms is now a partial envelope with C(3) being the deviant atom (by −0·12 Å) from the plane of C(3a), C(7a), C(1) and O(2). The six-membered lactone ring, which was described as a boat in (4), is now a very twisted boat. The isolated ring is interesting. In both (4) and (1) a simple chair conformation is adopted. However, comparison of the bond angles shows very significant differences of up to 8° in the vicinity of

C(3″) between the two compounds. It is difficult to imagine an electronic reason for the difference, and it is not obvious that intermolecular steric interactions are directly responsible since there are no particularly close approaches to atoms associated with that ring for either compound.

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Structure of (*Z*)-3-Methoxycarbonylamino-*N*,*N*-dimethyl-2-phenylpropenamide

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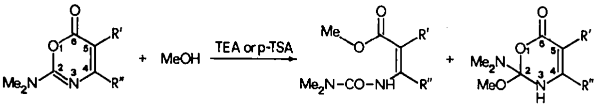
Abstract. $C_{13}H_{16}N_2O_3$, $M_r = 248{\cdot}3$, monoclinic, $P2_1/c$, $a = 10{\cdot}750\,(1)$, $b = 13{\cdot}039\,(1)$, $c = 10{\cdot}104\,(1)$ Å, $\beta = 113{\cdot}17\,(1)°$, $V = 1302{\cdot}0(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}267$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å (graphite-crystal monochromator), $\mu = 0{\cdot}85$ cm^{-1}, $F(000) = 528$, room temperature, final $R = 0{\cdot}047$ for 2212 observed reflections. The dimethylamido group is tilted by about 70° with respect to the rest of the molecule; both dimethylamido and *N*-carboxymethyl-*N*-vinylamino groups are extensively conjugated. The molecules are strongly linked by an N—H···O hydrogen bond through a centre of symmetry, and the crystal packing is based on an H-bond network.

Introduction. Beccalli, Marchesini & Molinari (1986, hereafter BMM) studied the alcoholysis of several 2-dimethylamino-1,3-oxazin-6-ones (I). They always obtained a mixture of two products to which structures (II) and (III) were attributed, respectively. Later, BMM had some doubts on the nature of (III); for this reason, this work was carried out to check the structural formula of the second product of the reaction. The particular compound studied here was chosen because its crystals were suitable for the X-ray crystal analysis.



(I) (II) (III)

Experimental. A crystal measuring $0{\cdot}25 \times 0{\cdot}20 \times 0{\cdot}18$ mm was selected and mounted on a CAD-4 diffractometer. The cell parameters were obtained from least-squares fit of 25 reflections in the range $14 < \theta < 19°$; 2976 unique reflections [2212 with $I > \sigma(I)$] were measured up to $2\theta = 55°$, $h\,0\to13$, $k\,0\to16$, $l\,-13\to11$, with ω–2θ scan technique, and corrected for Lorentz and polarization effects, but not for absorption. Three standard reflections showed no significant intensity variation. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All H-atom positions were located from a difference Fourier synthesis and included isotropically in final anisotropic refinement based on F, with $w = 4F_o^2/[\sigma(F_o^2) + 0{\cdot}0004F_o^4]$. Final $R = 0{\cdot}047$, $wR = 0{\cdot}040$, $S = 1{\cdot}6$, max. residual density $0{\cdot}2$ e Å^{-3}, max. shift $0{\cdot}05\sigma$ on final cycle, extinction coefficient $g = 15(1) \times 10^{-6}$ [Larson (1967), equation (3)]. Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs used include *SDP* (Enraf–Nonius, 1979), *ORTEP*II (Johnson, 1976), *PARST* (Nardelli, 1983) and various in-house programs for refinement and geometrical analysis running on a Gould 32/97 computer.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* bond distances and angles and selected torsion angles in Table 2.

As Fig. 1 shows, the title compound does not have the structure (III). Formally, the true structure is obtained by shifting the dimethylamino group from

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44168 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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