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Structure of Dihydrodecompostin

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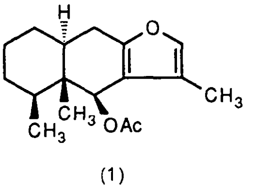
Abstract. $C_{17}H_{22}O_4$, $M_r = 290.36$, monoclinic, $P2_1$, $a = 7.197\,(1)$, $b = 8.174\,(1)$, $c = 13.649\,(1)$ Å, $\beta = 103.10\,(1)^\circ$, $V = 728.1$ Å^3, $Z = 2$, $D_x = 1.233$ g cm^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1.5418$ Å, $\mu = 6.92$ cm^{-1}, $F(000) = 312$, room temperature, $R = 0.057$ for 1168 unique observed reflections. The crystallographic analysis confirms the structure previously assigned to dihydrodecompostin on the basis of spectral data and chemical evidence. In addition it establishes an (S) configuration at C6 for the title compound.

Introduction: Plants belonging to the Senecioneae tribe (genus *Euryops, Othona, Senecio* and *Ligularia*) contain a variety of furanoeremophilane compounds (Bohlmann, Zdero & Grez, 1974; Moriyama, Sato, Nagano, Tanahashi & Takahashi, 1972). It has been reported that another member of the same tribe, *Tetradymia glabrata*, contained furanoeremophilenic compounds which were subsequently shown to be hepatotoxic substances responsible for the death of sheep feeding on the plant (Jennings, Hurley, Reeder, Holian, Lee, Caughlan & Larsen, 1976).

We have isolated the related compound 6β-acetoxy-9-oxo-furanoeremophilane (dehydrodecompostin) from *Senecio patagonicus*, as the main metabolite of the plant. Included in this report is the X-ray analysis of the title compound (1), which confirms the structure previously assigned on the basis of spectral data and chemical evidence (Villarroel, Torres, Gavin, Reina & de la Fuente, 1991) and establishes the absolute configuration as (6S,4S,5S,10R).



(1)

Experimental. Crystals were grown from methanol. Data were collected with a Siemens AED diffractometer using graphite-monochromated Cu $K\alpha$ radiation; approximate crystal dimensions 0.4 × 0.2 × 0.2 mm. Lattice parameters and their e.s.d.'s were derived from the setting angles of 13 reflections with $3 \le 2\theta \le 40^\circ$. Intensity data for 1615 reflections (h 0:8, k 0:9, l − 14:14; $2 \le 2\theta \le 120^\circ$) were collected in the ω/θ scan mode, 1238 unique, 1168 observed reflections [$I \ge 3\sigma(I)$]. Two reference reflections (020, $12\bar{1}$) measured every hour showed no significant decrease during the exposure. The intensity data were corrected for Lp effects. The space group was derived from the systematic absences. Structure solved by direct methods (*SHELXS*86; Sheldrick, 1986). Refinement by full-matrix least squares (*XRAY*80; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1980), anisotropic thermal parameters for all non-H atoms. The H atoms were placed in calculated positions (C—H distance 1.00 Å) (*HSEARCH*; Fayos & Martínez-Ripoll, 1980) and included in the final refinement as a fixed isotropic contribution. A weighting scheme [$w = k/|f(F_o)|^2 f(\sin\theta/\lambda)$] was chosen to obtain flat dependence of ΔF versus F_o and $\sin\theta/\lambda$ (*PESOS*; Martínez-Ripoll & Cano, 1980). The final discrepancy indices for the correct enantiomer are $R = 0.057$ and $wR = 0.071$. Maximum Δ/σ in the final refinement cycle was 0.076, maximum electron density in the final difference Fourier synthesis 0.17 e Å^{-3}. The absolute configuration was determined as (6S,4S,5S,10R) by comparison of 32 Bijvoet pairs with $F_o \ge 10\sigma(F_o)$ which are in the ranges $5 \le F_o \le 50$ and $0.15 \le \sin\theta/\lambda \le 0.40$ Å^{-1} (*CONFAB*; Martínez-Ripoll & Fayos, 1980). The average Bijvoet differences are 0.483 for the correct enantiomer *versus* 0.495 for the incorrect enantiomer. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); geometrical calculations using *PARST* (Nardelli, 1982).

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Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* ($Å^2$) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	−0.3700 (5)	−0.5574	−0.9406 (3)	62 (1)
O2	−0.3437 (5)	−0.2678 (8)	−0.8171 (3)	69 (1)
O3	0.2313 (5)	−0.7059 (7)	−0.7835 (3)	48 (1)
O4	0.2539 (7)	−0.9122 (7)	−0.6719 (4)	79 (2)
C1	−0.0681 (8)	−0.2298 (9)	−0.6395 (4)	56 (2)
C2	0.0681 (9)	−0.2464 (10)	−0.5370 (4)	67 (2)
C3	0.2609 (8)	−0.3024 (10)	−0.5499 (4)	60 (2)
C4	0.2578 (7)	−0.4621 (8)	−0.6087 (3)	44 (2)
C5	0.1123 (6)	−0.4592 (8)	−0.7115 (3)	36 (1)
C6	0.0692 (6)	−0.6367 (8)	−0.7508 (3)	37 (1)
C7	−0.0985 (7)	−0.6472 (8)	−0.8386 (3)	43 (2)
C8	−0.2321 (7)	−0.5254 (9)	−0.8558 (3)	49 (2)
C9	−0.2320 (7)	−0.3841 (9)	−0.7948 (4)	47 (2)
C10	−0.0831 (6)	−0.3917 (8)	−0.6961 (3)	41 (2)
C11	−0.1587 (8)	−0.7654 (10)	−0.9155 (4)	56 (2)
C12	−0.3205 (9)	−0.7074 (11)	−0.9746 (4)	66 (2)
C13	−0.0710 (11)	−0.9285 (10)	−0.9294 (5)	75 (3)
C14	0.1852 (7)	−0.3538 (9)	−0.7878 (4)	47 (2)
C15	0.4668 (7)	−0.4958 (10)	−0.6141 (4)	63 (2)
C16	0.3108 (8)	−0.8447 (8)	−0.7369 (5)	57 (2)
C17	0.4764 (10)	−0.8974 (11)	−0.7799 (7)	91 (3)

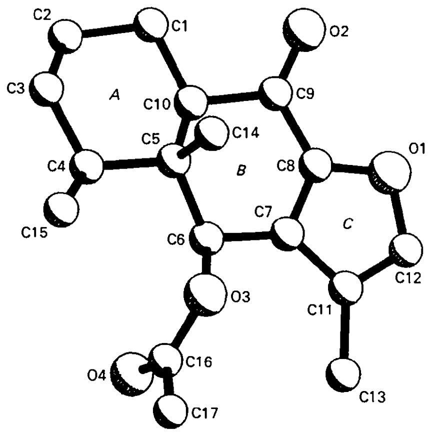

Fig. 1. Structure of the title compound showing the atom-numbering scheme.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

O1—C8	1.369 (5)	C5—C6	1.553 (9)
O1—C12	1.386 (9)	C5—C10	1.569 (7)
O2—C9	1.238 (8)	C5—C14	1.532 (8)
O3—C6	1.455 (7)	C6—C7	1.498 (6)
O3—C16	1.362 (8)	C7—C8	1.366 (9)
O4—C16	1.194 (9)	C7—C11	1.420 (8)
C1—C2	1.523 (7)	C8—C9	1.424 (9)
C1—C10	1.524 (10)	C9—C10	1.521 (6)
C2—C3	1.509 (9)	C11—C12	1.344 (8)
C3—C4	1.530 (10)	C11—C13	1.506 (11)
C4—C5	1.550 (6)	C16—C17	1.505 (11)
C4—C15	1.547 (7)		

C8—O1—C12	105.1 (4)	C6—C7—C8	120.2 (5)
C6—O3—C16	117.5 (4)	C8—C7—C11	106.5 (5)
C2—C1—C10	110.2 (5)	O1—C8—C7	110.7 (4)
C1—C2—C3	109.7 (5)	C7—C8—C9	125.7 (5)
C2—C3—C4	114.6 (5)	O1—C8—C9	123.6 (4)
C3—C4—C15	106.1 (5)	O2—C9—C8	124.4 (5)
C3—C4—C5	112.9 (5)	C8—C9—C10	113.1 (5)
C5—C4—C15	115.1 (4)	O2—C9—C10	122.5 (6)
C4—C5—C14	111.0 (4)	C5—C10—C9	111.6 (4)
C4—C5—C10	109.0 (4)	C1—C10—C9	111.6 (5)
C4—C5—C6	109.9 (4)	C1—C10—C5	114.2 (5)
C10—C5—C14	110.4 (4)	C7—C11—C13	129.0 (5)
C6—C5—C14	111.3 (4)	C7—C11—C12	106.4 (6)
C6—C5—C10	105.0 (4)	C12—C11—C13	124.6 (5)
O3—C6—C5	110.9 (4)	O1—C12—C11	111.4 (5)
C5—C6—C7	113.0 (5)	O3—C16—O4	123.7 (6)
O3—C6—C7	106.8 (4)	O4—C16—C17	126.4 (7)
C6—C7—C11	133.3 (5)	O3—C16—C17	110.0 (6)

C10—C1—C2—C3	57.3 (7)	O4—C16—O3—C6	−0.5 (9)
C10—C5—C6—O3	171.0 (4)	C17—C16—O3—C6	−179.6 (5)
C7—C8—O1—C12	1.6 (6)	C11—C7—C8—O1	−1.7 (6)
O1—C11—C12—C13	177.3 (6)	O1—C9—C8—O2	−8.0 (9)
C1—C9—C10—O2	−9.7 (8)		

Discussion. Final positional parameters are reported in Table 1.* The molecular structure for the correct enantiomer of the title compound including the atom-numbering scheme is illustrated in Fig. 1. Bond distances, bond angles and relevant torsion angles are shown in Table 2. The molecule presents a tricyclic skeleton with the central six-carbon ring (*B*) *trans*-fused to another six-carbon ring (*A*) and to the furano moiety (*C*). The equatorial methyl group on C4 and the axial methyl group on C5 have a *cis* relationship and are both β-oriented. The equatorial acetoxy group on C6 of ring *B* is also β-oriented. Ring *C* is planar with a maximum deviation from its least-squares plane of 0.011 (5) Å for the C8 atom. Ring *A* exhibits a slightly distorted chair ($^1C_4$) conformation as shown by the ring-puckering parameters (Cremer & Pople, 1975): $Q = 0.551$ (7), $q_2 = 0.055$ (7), $q_3 = -0.549$ (7) Å, $\varphi_2 = -161.8$ (6) and $\theta = 174.3$ (7)° for the sequence C1, C2, C3, C4, C5, C10 with C1 and C4 displaced 0.676 (7) and −0.599 (6) Å from the best plane through C2, C3, C5 and C10. Ring *B* is in a conformation between half-chair ($^5H_{10}$) and envelope (^5E) as shown by the torsion angles C6—C7—C8—C9 [−1.8 (9)°] and C7—C8—C9—C10 [−9.3 (8)°] and the ring-puckering parameters: $Q = 0.534$ (5), $q_2 = 0.419$ (6), $q_3 = -0.332$ (5) Å, $\varphi_2 = 161.5$ (7) and $\theta = 128.4$ (6)° for the sequence C5, C6, C7, C8, C9, C10 with the C5 and C10 atoms displaced 0.550 (5) and −0.261 (5) Å from the plane defined by C6, C7, C8 and C9. Average values for distances are C(sp^3)—C(sp^3) 1.539 (8), C(sp^3)—C(sp^2) 1.508 (9), C═C 1.355 (9), C(sp^3)—O 1.455 (7), C(sp^2)—O 1.376 (7) and C═O 1.217 (9). The valence angles involving tetrahedral and trigonal C atoms have mean values

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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 54465 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of 111.0 (4) and 125.3 (5)° respectively. The crystal packing is governed by van der Waals interactions.

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Structures of 6-Amino-1,3-dimethyl-5-nitrosouracil Monohydrate and 6-Amino-5-formyl-1,3-dimethyluracil Monohydrate

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Abstract. 6-Amino-1,3-dimethyl-5-nitroso-2,4(1*H*,3*H*)-pyrimidinedione monohydrate (DANU), $C_6H_8N_4O_2.H_2O$, $M_r = 202.17$, orthorhombic, *Pnam*, $a = 13.978\,(10)$, $b = 9.638\,(8)$, $c = 6.338\,(11)$ Å, $V = 853.9$ Å^3, $Z = 4$, $D_x = 1.57$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.88$ cm^{-1}, $F(000) = 424$, $T = 293$ K, $R = 0.043$ for 709 unique observed reflections [$F_o > 6\sigma(F)$]. 6-Amino-5-formyl-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione monohydrate (DAFU), $C_7H_9N_3O_2.H_2O$, $M_r = 201.18$, monoclinic, *C*2/*c*, $a = 15.557\,(11)$, $b = 7.562\,(11)$, $c = 16.972\,(13)$ Å, $\beta = 116.69\,(5)°$, $V = 1783.88$ Å^3, $Z = 8$, $D_x = 1.50$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.81$ cm^{-1}, $F(000) = 848$, $T = 293$ K, $R = 0.056$ for 718 unique observed reflections [$F_o > 6\sigma(F)$]. The molecular structures of the free uracil derivatives investigated are similar to those found for similar derivatives of uracil whose structures have been determined as ligands in various metal complexes.

Introduction. This investigation is part of a series of structural studies of pyrimidine derivatives, in this case with amino substituents on C6. The aim of these studies is to elucidate the role that metal–pyrimidine complexes play in biological systems. To date the structures of several metal complexes (Moreno, Salas, Colacio, Sánchez & Nieto, 1986; Romero, Moreno, Ruiz, Sánchez & Nieto, 1986; Romero-Molina, Gutiérrez-Valero, López-Garzón, Salas-Peregrín, Arriortúa-Marcaida & Zuñiga, 1987; García-Megías, Colacio-Rodríguez, García-Rodríguez, Salas-Peregrín, Simard & Beauchamp, 1989; Kivekäs, Colacio, Ruiz, López-González & León, 1989; Suárez-Varela, Legros, Galy, Colacio-

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