Kepert, D. L., Patrick, J. M., Skelton, B. W. & White, A. H. (1988). *Aust. J. Chem.* **41**, 157–158.
Kepert, D. L., Skelton, B. W. & White, A. H. (1994). *Aust. J. Chem.* **47**, 391–396.
Matković-Čalogović, D., Popović, Z. & Korpar-Čolig, B. (1995). *J. Chem. Crystallogr.* **25**, 453–458.
Rizzoli, C., Sangermano, V., Calestani, G. & Andreetti, G. D. (1987). *J. Appl. Cryst.* **20**, 436–439.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1993). *PLUTON93. Program for the Display and Analysis of Crystal and Molecular Structures.* University of Utrecht, The Netherlands.
Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Version 7.09. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Version 7.03. Stoe & Cie, Darmstadt, Germany.
Thomas, N. C. & Fischer, J. (1990). *J. Coord. Chem.* **21**, 119–128.
Vicković, I. (1988). *J. Appl. Cryst.* **21**, 987–990.
Vicković, I. (1994). *J. Appl. Cryst.* **27**, 437–437.

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An 18-Chloro-4α-hydroxy Derivative of 19-Acetylteupolin IV: a Neo-clerodane Diterpenoid of Biological Interest

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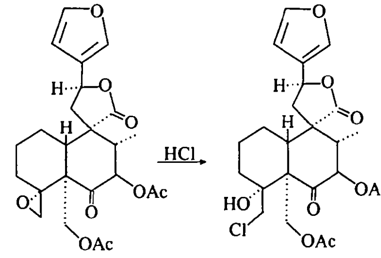
Abstract

The title compound, (12*S*)-7β,19-diacetoxy-18-chloro-15,16-epoxy-4α-hydroxy-6-oxo-neo-cleroda-13(16),14-dien-20,12-olide {systematic name: 4′a-(acetoxymethyl)-5′-(chloromethyl)-5-(3-furyl)-5′-hydroxy-2′-methyl-2,4′-dioxodecahydrospiro[furan-3(2*H*),1′(2′*H*)naphthalen]-3′-yl acetate; $C_{24}H_{29}ClO_9$}, is of interest on account of its biological activity as an insect antifeedant. The fused six-membered rings of the molecule have similar chair conformations. The crystal contains dimeric molecules which are formed *via* bifurcated (intra- and intermolecular) O—H···O hydrogen bonds.

Comment

A large number of diterpenoids with the clerodane skeleton have been isolated from plants in the past few years (Merritt & Ley, 1992). Interest in these compounds has been stimulated by their biological activity as antitumoural, antimicrobial and antifungal agents, and particularly as antifeedant agents against some economically important lepidopterous pests (Merritt & Ley, 1992; Simmonds & Blaney, 1992). The richest source of this kind of compound has been plants belonging to the genus *Teucrium* of the family Labiatae, from which about 170 clerodanes have been isolated (Merritt & Ley, 1992; Piozzi, 1994; Rodriguez *et al.*, 1994). Some years ago a new neo-clerodane (Rogers *et al.*, 1979), 19-acetylteupolin IV, (1), was isolated (De la Torre, Piozzi, Rizk, Rodriguez & Savona, 1986) and its structure and absolute configuration [(12*S*)-7β,19-diacetoxy-4α,18;15,16-diepoxy-6-oxo-neo-cleroda-13(16),14-dien-20,12-olide] were established by spectroscopic (^{1}H and ^{13}C NMR, CD) means and by comparison with closely related compounds. Compounds possessing 7β-acetoxy-6-oxo functional groups, however, are not usual among the natural neo-clerodanes (Merritt & Ley, 1992; Piozzi, 1994; Rodriguez-Hahn, Esquivel & Cardenas, 1994; Davies-Coleman, Hanson & Rivett, 1994) and in our opinion the structure attributed (De la Torre *et al.*, 1986) needed further support.



(1) (2)

Attempts at obtaining suitable crystals of (1) for X-ray diffraction analysis were unsuccessful. Treatment of the natural diterpenoid (1) with hydrochloric acid (Rodriguez *et al.*, 1994) gave the chlorohydrin (2) in almost quantitative yield.

Rings *A* and *B* (Fig. 1) have very similar chair conformations with the following Cremer & Pople (1975) parameters: q_2 = 0.035 (5), q_3 = 0.586 (5) Å, φ_2 = −116 (7) and θ_2 = 3.4 (5)° for ring *A*; q_2 = 0.021 (4), q_3 = 0.501 (4) Å, φ_2 = 178 (28) and θ_2 = 2.4 (5)° for ring *B*. The γ-lactone ring (*C*) has an envelope conformation, with the C11 atom deviating by −0.304 (4) Å from the plane defined by the other four atoms [maximum deviation of −0.029 (4) Å for atom C20]. Ring *D* is planar (all deviations are less than 0.004 Å). All interatomic distances and angles have normal values. The crystal packing involves an inter- and intramolecular bifurcated hydrogen bond through the H70 atom; O7···O5 2.946 (4) Å, O7—H70···O5 127.4 (3)°, O7···O5$^{\rm i}$ 3.030 (4) Å and O7—H70···O5$^{\rm i}$ 142.0 (3)° [symmetry code: (i) $1-x, y, 1-z$]. This links pairs of molecules through a twofold axis (Fig. 1).

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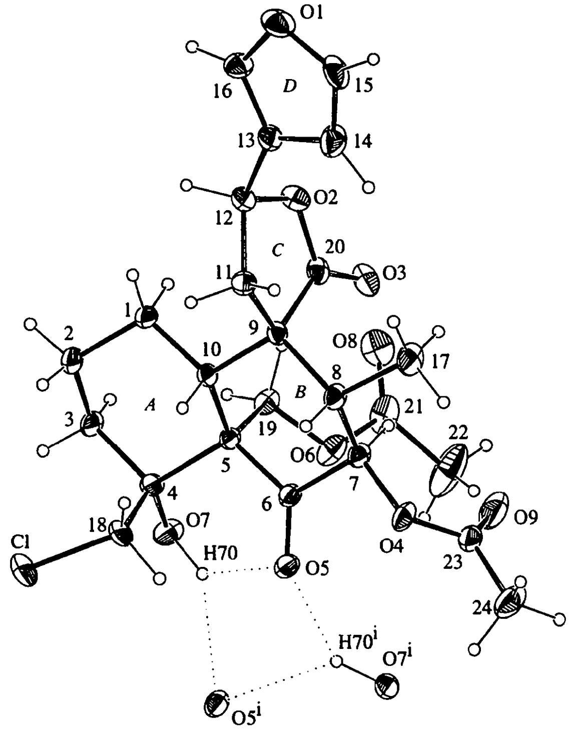

Fig. 1. The molecular structure, atomic- and ring-labelling schemes, and hydrogen-bonding scheme of (2). Displacement ellipsoids are drawn at the 30% probability level and C atoms are labelled by number only.

The results are in accordance with those already found spectroscopically for compound (1) and thus, taking into account the fact that (2) is merely a chemical transformation of (1), the structure previously assigned to 19-acetylteupolin IV (De la Torre *et al.*, 1986) is now established crystallographically.

Experimental

For details of the preparation of (2), see the preparation of compound (6) described in the work of Rodriguez *et al.* (1994). Crystals of (2) suitable for diffraction analysis were crystallized from EtOAc/petrol solution.

Crystal data

$C_{24}H_{29}ClO_9$
$M_r = 496.92$
Monoclinic
$C2$
$a = 25.348\,(3)$ Å
$b = 7.8824\,(7)$ Å
$c = 11.9280\,(10)$ Å
$\beta = 96.80\,(2)°$
$V = 2366.5\,(4)$ Å^3
$Z = 4$
$D_x = 1.395$ Mg m^{-3}
$D_m = 1.389$ Mg m^{-3}
D_m measured by flotation in benzene/bromoform

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 40 reflections
$\theta = 6$–$20°$
$\mu = 1.885$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.3 × 0.2 × 0.2 mm
Colourless

Data collection

Seifert XRD3000-*S* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.46$, $T_{\max} = 0.69$
2102 measured reflections
2102 independent reflections

1896 observed reflections $[I > 2\sigma(I)]$
$\theta_{\max} = 65.04°$
$h = -29 \rightarrow 29$
$k = 0 \rightarrow 8$
$l = -14 \rightarrow 13$
2 standard reflections monitored every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0522$
$wR(F^2) = 0.1322$
$S = 1.016$
2102 reflections
308 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1114P)^2 + 0.0012P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.308$ e Å^{-3}
$\Delta\rho_{\min} = -0.422$ e Å^{-3}

Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0041 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.02 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl	0.52274 (5)	−0.2529 (2)	0.19976 (11)	0.0820 (5)
O1	0.09647 (13)	0.0067 (5)	−0.0526 (3)	0.0716 (11)
O2	0.24311 (11)	0.2061 (4)	0.1277 (2)	0.0508 (7)
O3	0.28680 (12)	0.3253 (4)	0.2796 (3)	0.0578 (8)
O4	0.34617 (12)	−0.0305 (4)	0.5534 (2)	0.0518 (8)
O5	0.43800 (10)	−0.0232 (4)	0.4732 (2)	0.0490 (8)
O6	0.4175 (2)	0.3429 (5)	0.4015 (2)	0.0604 (9)
O7	0.50459 (10)	0.1156 (5)	0.3088 (2)	0.0571 (9)
O8	0.3817 (2)	0.5930 (5)	0.3479 (3)	0.0755 (10)
O9	0.3500 (2)	0.2212 (7)	0.6373 (3)	0.099 (2)
C1	0.36395 (14)	0.0588 (6)	0.0837 (3)	0.0428 (9)
C2	0.4171 (2)	0.0060 (7)	0.0459 (3)	0.0510 (11)
C3	0.46332 (13)	0.0759 (7)	0.1251 (3)	0.0493 (12)
C4	0.46178 (13)	0.0253 (6)	0.2492 (3)	0.0427 (9)
C5	0.40683 (13)	0.0853 (5)	0.2880 (3)	0.0354 (9)
C6	0.40111 (14)	0.0297 (5)	0.4081 (3)	0.0364 (8)
C7	0.34611 (14)	0.0484 (6)	0.4441 (3)	0.0399 (9)
C8	0.30141 (14)	−0.0332 (6)	0.3652 (3)	0.0411 (9)
C9	0.30233 (13)	0.0239 (5)	0.2413 (3)	0.0345 (8)
C10	0.36004 (12)	0.0071 (5)	0.2062 (3)	0.0345 (8)
C11	0.26314 (15)	−0.0842 (6)	0.1612 (3)	0.0415 (9)
C12	0.23411 (14)	0.0410 (6)	0.0768 (3)	0.0432 (9)
C13	0.17606 (15)	0.0149 (6)	0.0487 (3)	0.0470 (10)
C14	0.1376 (2)	−0.0299 (9)	0.1218 (4)	0.068 (2)
C15	0.0902 (2)	−0.0330 (9)	0.0581 (5)	0.076 (2)
C16	0.1486 (2)	0.0341 (7)	−0.0554 (4)	0.0557 (11)
C17	0.2481 (2)	0.0017 (8)	0.4103 (4)	0.0638 (14)
C18	0.4696 (2)	−0.1663 (8)	0.2665 (4)	0.0573 (12)
C19	0.4061 (2)	0.2820 (6)	0.2875 (3)	0.0414 (9)
C20	0.27874 (14)	0.2014 (6)	0.2222 (3)	0.0426 (9)
C21	0.4023 (3)	0.5013 (7)	0.4210 (5)	0.0658 (14)
C22	0.4157 (5)	0.5506 (10)	0.5418 (5)	0.137 (4)
C23	0.3478 (2)	0.0702 (9)	0.6434 (3)	0.0556 (13)
C24	0.3464 (2)	−0.0277 (12)	0.7491 (4)	0.088 (2)

Table 2. *Selected torsion angles (°)*

C1—C2—C3—C4	55.8 (5)	C5—C6—C7—C8	52.5 (5)
C2—C3—C4—C5	−56.5 (5)	C6—C7—C8—C9	−51.9 (5)
C3—C4—C5—C10	56.1 (4)	C7—C8—C9—C10	48.6 (5)
C4—C5—C10—C1	−57.6 (4)	C8—C9—C10—C5	−49.2 (5)
C5—C10—C1—C2	57.3 (5)	C9—C10—C5—C6	47.3 (4)
C10—C1—C2—C3	−55.0 (5)	C10—C5—C6—C7	−47.3 (5)

Data collection: Seifert XRD3000-*S* diffractometer software. Cell refinement: *LSUCRE* (Appleman, 1995). Data reduction: *XRAY*80 (Stewart, 1978). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, G., Guagliardi, A. & Polidori, G. (1992). *SIR92. Program for Crystal Structure Solution.* University of Bari, Italy.

Appleman, D. E. (1995). US Geological Survey, Washington, DC, USA. Unpublished results.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Davies-Coleman, M. T., Hanson, J. R. & Rivett, D. E. A. (1994). *Phytochemistry*, **36**, 1549–1550.

De la Torre, M. C., Piozzi, F., Rizk, A.-F., Rodriguez, B. & Savona, G. (1986). *Phytochemistry*, **25**, 2239–2240.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Merritt, A. T. & Ley, S. V. (1992). *Nat. Prod. Rep.* **9**, 243–287.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Piozzi, F. (1994). *Heterocycles*, **37**, 603–626.

Rodriguez, B., De la Torre, M. C., Perales, A., Malakov, P. Y., Papanov, G. Y., Simmonds, M. S. J. & Blaney, W. M. (1994). *Tetrahedron*, **50**, 5451–5468.

Rodriguez-Hahn, L., Esquivel, B. & Cardenas, J. (1994). *Prog. Chem. Org. Nat. Prod.* **63**, 107–196.

Rogers, D., Unal, G. G., Williams, D. J., Ley, S. V., Sim, G. A., Joshi, B. S. & Ravindranath, K. R. (1979). *J. Chem. Soc. Chem. Commun.* pp. 97–99.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Simmonds, M. S. J. & Blaney, W. M. (1992). *Advances in Labiatae Science*, edited by R. M. Harley & T. Reynolds, pp. 375–392. Kew, England: Royal Botanic Gardens.

Stewart, J. M. (1978). Editor. *The XRAY System of Crystallographic Programs.* Version of 1980. Technical Report TR-446. Computer Science Center, University of Maryland, College Park, Maryland, USA.

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Hydrogen Bonding in 4,4-Dimethylcyclohexane-1,3-dione and 2,5,5-Trimethylcyclohexane-1,3-dione Monohydrate

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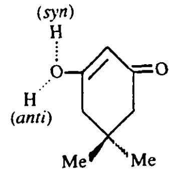
Abstract

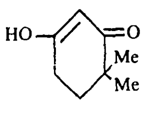
The enol of 4,4-dimethylcyclohexane-1,3-dione (3-hydroxy-6,6-dimethylcyclohex-2-en-1-one, $C_8H_{12}O_2$) forms hydrogen-bonded spiral chains like those in 5,5-dimethylcyclohexane-1,3-dione, except for disorder of the optical isomers. 2,5,5-Trimethylcyclohexane-1,3-dione monohydrate (enol form 3-hydroxy-2,5,5-trimethylcyclohex-2-en-1-one monohydrate, $C_9H_{14}O_2.H_2O$) forms hydrogen-bonded layers containing tetramolecular rings with a short OH· · ·water hydrogen bond [2.428 (4) Å].

Comment

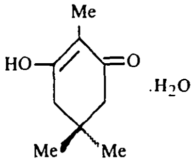
Since cyclohexane-1,3-dione (CHD) and its derivatives are extensively enolized [see (I) below], there are possibilities of >C—O—H· · ·O=C< hydrogen-bonded networks in the solid state. These networks can be involved in supramolecular structures such as the clathrate-like $(CHD)_6$–benzene structure (Etter, Urbanczyck-Lipkowska, Jahn & Frey, 1986) and the dimeric encapsulate $[Cr(C_6H_6)_2^+.(CHD)_4^-]_2$ (Braga, Grepioni, Bryne & Wolf, 1995). The intermolecular hydrogen bonds in these networks are relatively strong, with O· · ·O distances in the range 2.55–2.60 Å. In practice, the hydroxy proton in CHD derivatives is found close to the idealized *syn* or *anti* positions, indicated in (I) below. Similarly, the sp^2 positions of formal lone pairs of electrons on the



(I)



(II)



(III)

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