

Fig. 1. Stereoscopic view of the molecule with atomic numbering scheme (PLUTO; Motherwell & Clegg, 1978).

Related literature. The crystal structures of 1,3,5-triphenyl-1,3,5-perhydrotriazine-2,4,6-trione (Usanmaz, 1979) and 1,3,5-tribenzamido-1,3,5-

hexahydrotriazine monohydrate (George & Gilardi, 1987) are closely related to the title compound.

References

- GEORGE, C. & GILARDI, R. (1987). *Acta Cryst.* C43, 1003–1005.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
USANMAZ, A. (1979). *Acta Cryst.* B35, 1117–1119.

Acta Cryst. (1990). C46, 1170–1172

Structure of a Neoclerodane Dilactone from *Baccharis rhomboidalis*

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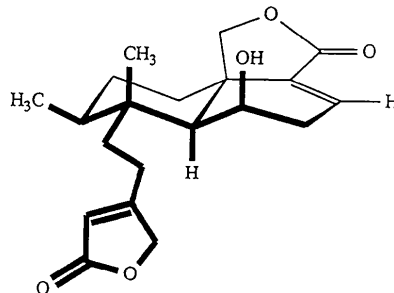
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(Received 8 December 1989; accepted 30 January 1990)

Abstract. 1-Hydroxyneoclerodane-3,13-diene-15,16;-19,20-diolide, C₂₀H₂₆O₅, *M_r* = 346.42, orthorhombic, *P*2₁2₁2₁, *a* = 15.601 (4), *b* = 15.962 (4), *c* = 7.093 (2) Å, *V* = 1766.3 Å³, *Z* = 4, *D_x* = 1.303 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.09 mm⁻¹, *F*(000) = 744, *T* = 293 K, final *R* = 0.064 for 1430 unique observed reflections with *F* > 3σ(*F*). The molecular structure of the title compound consists of two *trans*-fused six-membered rings with a butenolide ring fused to both, and possesses as substituents a secondary and tertiary methyl group at C(8) and C(9), respectively, a secondary hydroxyl group at C(1), and a side chain with an α,β-unsaturated γ-lactone group at C(9). The methyl and hydroxyl groups and C(19) are in *cis*-axial configuration in agreement with the molecular structure proposed previously on the basis of chemical and spectroscopic methods [San-Martin, Rovirosa, Labbé, Givovich, Mahú & Castillo (1986). *Phytochemistry*, 25, 1393–1395]. All bond lengths and angles are within the expected ranges.

Experimental. In the course of our chemical investigations of the genus *Baccharis*, the title neoclerodane dilactone was isolated from *Baccharis rhomboidalis* Remy from Central Chile. Colourless crystals, 0.5 ×



0.5 × 1.0 mm, were used for X-ray analysis; Huber computer-controlled four-circle diffractometer, graphite-monochromated Mo *K*α radiation, ω-scan mode; cell parameters by least squares from 26 centred reflections, 2θ ≤ 50°; 1539 unique reflections

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters 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	$U_{eq}(\text{\AA}^2)$
O(1)	9758 (3)	6786 (5)	3386 (8)	62 (2)
C(1)	10243 (4)	6606 (4)	1716 (9)	44 (2)
O(2)	12685 (3)	2997 (3)	560 (8)	75 (2)
C(2)	10500 (4)	7428 (4)	707 (11)	59 (3)
O(3)	7585 (3)	7289 (3)	463 (7)	61 (2)
C(3)	9702 (4)	7877 (3)	21 (10)	55 (3)
C(4)	8997 (4)	7464 (3)	-386 (10)	43 (2)
C(5)	8866 (3)	6526 (3)	-229 (8)	34 (2)
C(6)	8595 (4)	6142 (3)	-2159 (9)	47 (2)
C(7)	8464 (4)	5192 (4)	-1931 (11)	54 (3)
C(8)	9263 (4)	4728 (3)	-1161 (10)	46 (2)
C(9)	9609 (3)	5132 (3)	759 (9)	36 (2)
C(10)	9711 (3)	6078 (3)	328 (8)	33 (2)
C(11)	10476 (3)	4719 (3)	1270 (9)	46 (2)
C(12)	11213 (3)	4829 (3)	-144 (9)	47 (2)
C(13)	11944 (4)	4255 (3)	257 (9)	39 (2)
C(14)	12747 (4)	4414 (4)	570 (10)	54 (3)
O(15)	13983 (3)	3541 (3)	1084 (7)	94 (2)
C(15)	13232 (5)	3644 (5)	796 (11)	63 (3)
C(16)	11837 (4)	3322 (4)	276 (11)	62 (3)
C(17)	9001 (4)	4948 (3)	2410 (9)	53 (3)
C(18)	9050 (4)	3797 (3)	-1004 (12)	80 (3)
C(19)	8076 (3)	6558 (3)	1080 (10)	46 (2)
O(20)	7895 (3)	8549 (3)	-810 (8)	89 (2)
C(20)	8139 (5)	7859 (5)	-309 (12)	62 (3)

Table 2. Interatomic distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

O(1)—H(1)	0.548 (78)	O(1)—C(1)	1.434 (9)
C(1)—C(2)	1.548 (9)	C(1)—C(10)	1.539 (8)
O(2)—C(15)	1.351 (9)	O(2)—C(16)	1.434 (8)
C(2)—C(3)	1.516 (9)	O(3)—C(19)	1.463 (7)
O(3)—C(20)	1.368 (9)	C(3)—C(4)	1.315 (9)
C(4)—C(5)	1.515 (8)	C(4)—C(20)	1.480 (9)
C(5)—C(6)	1.558 (9)	C(5)—C(10)	1.551 (7)
C(5)—C(19)	1.545 (8)	C(6)—C(7)	1.538 (8)
C(7)—C(8)	1.550 (8)	C(8)—C(9)	1.601 (9)
C(8)—C(18)	1.526 (8)	C(9)—C(10)	1.549 (7)
C(9)—C(11)	1.548 (8)	C(9)—C(17)	1.535 (9)
C(11)—C(12)	1.536 (8)	C(12)—C(13)	1.490 (8)
C(13)—C(14)	1.297 (8)	C(13)—C(16)	1.499 (8)
C(14)—C(15)	1.452 (10)	O(15)—C(15)	1.201 (9)
O(20)—C(20)	1.220 (9)		
H(1)—O(1)—C(1)	97.0 (2)	O(1)—C(1)—C(2)	110.4 (5)
O(1)—C(1)—C(10)	110.7 (5)	C(2)—C(1)—C(10)	107.9 (5)
C(15)—O(2)—C(16)	108.9 (5)	C(1)—C(2)—C(3)	109.7 (5)
C(19)—O(3)—C(20)	108.6 (5)	C(2)—C(3)—C(4)	121.3 (5)
C(3)—C(4)—C(5)	126.3 (6)	C(3)—C(4)—C(20)	122.3 (6)
C(5)—C(4)—C(20)	107.2 (5)	C(4)—C(5)—C(6)	111.1 (5)
C(4)—C(5)—C(10)	111.1 (4)	C(6)—C(5)—C(10)	105.8 (4)
C(4)—C(5)—C(19)	96.9 (4)	C(6)—C(5)—C(19)	109.0 (4)
C(10)—C(5)—C(19)	122.7 (5)	C(5)—C(6)—C(7)	109.4 (5)
C(6)—C(7)—C(8)	113.7 (5)	C(7)—C(8)—C(9)	112.2 (5)
C(7)—C(8)—C(18)	108.4 (5)	C(9)—C(8)—C(18)	113.8 (6)
C(8)—C(9)—C(10)	105.0 (5)	C(8)—C(9)—C(11)	108.8 (4)
C(10)—C(9)—C(17)	111.8 (4)	C(8)—C(9)—C(17)	111.3 (4)
C(10)—C(9)—C(17)	113.6 (4)	C(11)—C(9)—C(17)	106.3 (5)
C(1)—C(10)—C(5)	111.6 (4)	C(1)—C(10)—C(9)	117.6 (5)
C(5)—C(10)—C(9)	114.3 (4)	C(9)—C(10)—C(12)	116.9 (5)
C(11)—C(12)—C(13)	112.2 (5)	C(12)—C(13)—C(14)	130.6 (5)
C(12)—C(13)—C(16)	121.9 (5)	C(14)—C(13)—C(16)	107.5 (5)
C(13)—C(14)—C(15)	110.9 (6)	O(2)—C(15)—C(14)	107.7 (6)
O(2)—C(15)—O(15)	122.2 (7)	C(14)—C(15)—O(15)	130.1 (7)
O(2)—C(16)—C(13)	104.9 (5)	O(3)—C(19)—C(5)	105.3 (5)
O(3)—C(19)—C(4)	107.7 (6)	O(3)—C(20)—O(20)	121.3 (6)
C(4)—C(20)—O(20)	131.0 (7)		

of which 1430 were treated as observed with $F > 3\sigma(F)$; two standard reflections (080, 0 $\bar{8}$ 0) every 100 measurements showed 0.6% variation in intensity. Diffraction intensities were measured up to $(\sin\theta)/\lambda = 0.59 \text{ \AA}^{-1}$ in the index range $h = 0 \rightarrow 18$, $k = 0 \rightarrow 18$ and $l = 0 \rightarrow 8$. ψ -scan absorption correction was applied. The structure was solved by direct phase determination using *SHELXTL-Plus* (Sheldrick, 1988), full-matrix least squares minimized $\sum w(\Delta F)^2$; H-atom positions were calculated geometrically and were fixed with isotropic displacement parameters $U_{iso} = 1.2U_{eq}$ of the bonded C. All other atoms, except H(1), were refined anisotropically. The final R values are $R = 0.064$ and $wR = 0.055$ for 1430 observed data and 230 variable parameters, $S = 3.51$, where $w^{-1} = \sigma^2(F)$. Final $(\Delta/\sigma)_{max} = 0.10$, $\Delta\rho_{max} = 0.24$ and $\Delta\rho_{min} = -0.27 \text{ e \AA}^{-3}$ on final difference Fourier map. Atomic scattering factors were taken from *SHELXTL-Plus*. Atomic coordinates and interatomic distances and angles are given in Tables 1 and 2, respectively. The molecule and the atom labelling are shown in Fig. 1.*

Related literature. For chemical investigations of the genus *Baccharis* see Herz, Pilotti, Soderholm, Shuhama & Vichnewski (1977), Bohmann, Zdero,

* Lists of structure factors, hydrogen atomic coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52650 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

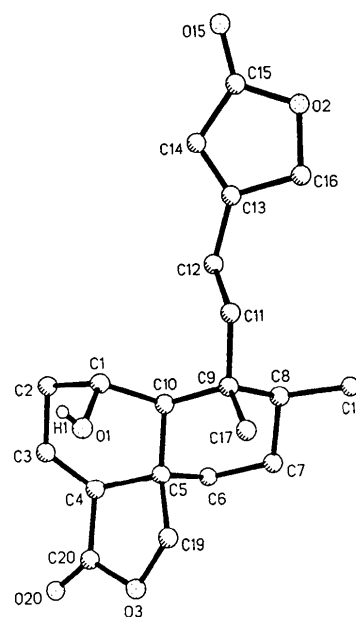


Fig. 1. A perspective drawing of the molecule with the atoms numbered according to the tables.

Grenz, Dhar, Robinson & King (1981), Bohlmann, Kramp, Grenz, Robinson & King (1981), Bohlmann, Kramp, Jakupovic, Robinson & King (1982), Gianello & Giordano (1984) and Soriano-García, Toscano, Esquivel, Hernández & Rodríguez-Hahn (1987). For chemical investigations of the genus *Baccharis* from Chile see San-Martin, Givovich & Castillo (1986), Givovich, San-Martin & Castillo (1986), San-Martin, Roviroso, Labbé, Givovich, Mahú & Castillo (1986), Gambaro, Chamy, Garbarino, San-Martin & Castillo (1986) and Gambaro, Chamy & Garbarino (1987).

References

BOHLMANN, F., KRAMP, W., GRENZ, M., ROBINSON, H. & KING, R. M. (1981). *Phytochemistry*, **20**, 1907–1910.
BOHLMANN, F., KRAMP, W., JAKUPOVIC, J., ROBINSON, H. & KING, R. M. (1982). *Phytochemistry*, **21**, 399–402.

BOHLMANN, F., ZDERO, C., GRENZ, M., DHAR, A. K., ROBINSON, H. & KING, R. M. (1981). *Phytochemistry*, **20**, 281–286.
GAMBARO, V., CHAMY, C. & GARBARINO, J. (1987). *Phytochemistry*, **26**, 475–477.
GAMBARO, V., CHAMY, C., GARBARINO, J., SAN-MARTIN, A. & CASTILLO, M. (1986). *Phytochemistry*, **25**, 2175–2177.
GIANELLO, J. & GIORDANO, O. (1984). *Rev. Latinoam. Quim.* **15**, 84–87.
GIVOVICH, A., SAN-MARTIN, A. & CASTILLO, M. (1986). *Phytochemistry*, **25**, 2829–2831.
HERZ, W., PILOTTI, A.-M., SODERHOLM, A.-C., SHUHAMA, I. K. & VICHNEWSKI, W. (1977). *J. Org. Chem.* **42**, 3913–3917.
SAN-MARTIN, A., GIVOVICH, A. & CASTILLO, M. (1986). *Phytochemistry*, **25**, 264–266.
SAN-MARTIN, A., ROVIROSA, J., LABBÉ, C., GIVOVICH, A., MAHÚ, M. & CASTILLO, M. (1986). *Phytochemistry*, **25**, 1393–1395.
SHELDRIK, G. M. (1988). *SHELXTL-Plus*, release 3.4. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Federal Republic of Germany.
SORIANO-GARCÍA, M., TOSCANO, R. A., ESQUIVEL, B., HERNÁNDEZ, M. & RODRÍGUEZ-HAHN, L. (1987). *Acta Cryst.* **C43**, 272–274.

Acta Cryst. (1990). **C46**, 1172–1174

Structure of 3-Hydroxy-1-methyl-1,3,5(10)-estratriene-11,17-dione

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(Received 10 November 1989; accepted 16 January 1990)

Abstract. $C_{19}H_{22}O_3$, $M_r = 298.39$, orthorhombic, $P2_12_12_1$, $a = 11.332$ (6), $b = 14.596$ (7), $c = 9.567$ (4) Å, $V = 1582.6$ (5) Å³, $Z = 4$, $D_x = 1.252$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.0778$ mm⁻¹, $F(000) = 640$, $T = 273$ K, $R = 0.067$ for 1762 unique observed reflections where $F > 2\sigma(F)$. The structure was studied to observe the effect of 1-methyl and 11-keto substitution. The 3-hydroxyl is hydrogen bonded to O11 at 2.76 Å. The B ring is in a $7\alpha,8\beta$ half-chair conformation. The molecule twists about the C(9)—C(10) bond to relieve the steric interaction between the 1-methyl and 11-keto groups. The C1—C10—C9—C11 torsion angle is 55 vs 33.5°, the average of 38 estradiol analogue structures.

Experimental. Rectangular rod-shaped crystals by evaporation from methanol, 0.18 × 0.20 × 0.30 mm,

Nicolet P3 diffractometer. ω -scan method, lattice parameters from the 2θ values of 24 reflections with $19 < 2\theta < 28^\circ$, intensity measurements performed up to $2\theta = 60^\circ$; range of hkl 0 to 16, -1 to 21, 0 to 14; variable scan speed from 3 to $30^\circ \text{ min}^{-1}$ (2θ). Four standard reflections (442, 620, 280, 015) varied in intensity by 2% throughout the experiment. 3746 reflections measured, 2627 unique reflections, $R_{\text{int}} = 0.018$, 1762 observed reflections with $F > 2\sigma(F)$.

Structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Hydrogens found from difference map and refined with isotropic displacement parameters; final $R = 6.7\%$, $wR = 5.7\%$, $S = 1.78$, $(\Delta/\sigma)_{\text{max}} = 0.17$. Weighting scheme based on estimates of experimental errors from counting statistics was used to calculate w . $(\Delta\rho)_{\text{max}} = 0.5 \text{ e } \text{Å}^{-3}$, $(\Delta\rho)_{\text{min}} = -0.3 \text{ e } \text{Å}^{-3}$ from final difference Fourier synthesis. No corrections for absorption or extinction were made. Atomic scattering factors were taken

† Deceased.