

References

- CLÉMENCE, F., JOLIVEAU-MAUSHART, C., MEIER, J., CEREDA, J., DELEVALLÉE, F., BENZONI, J. & DERAEDT, R. (1985). *Eur. J. Med. Chem. Chim. Ther.* **20**(3), 257–266.
- COTRAIT, M., DESTRADE, C. & GASPAROUX, H. (1977). *Mol. Cryst. Liq. Cryst.* **39**, 159–172.
- CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV, edited by J. A. IBERS & W. C. HAMILTON. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- GOLDSTEIN, P., LADELL, J. & BOWITZ, G. A. (1969). *Acta Cryst.* **B25**, 135–139.
- IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MAGOMODOVA, N. S. & ZVONKOVA, Z. N. (1980). *Kristallografiya*, **25**, 1183–1187.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1986). **C42**, 1440–1442

A Hemiacetal Derivative of a *cis*-Clerodane Diterpene

BY IRAJ TAVANAIEPOUR AND WILLIAM H. WATSON*

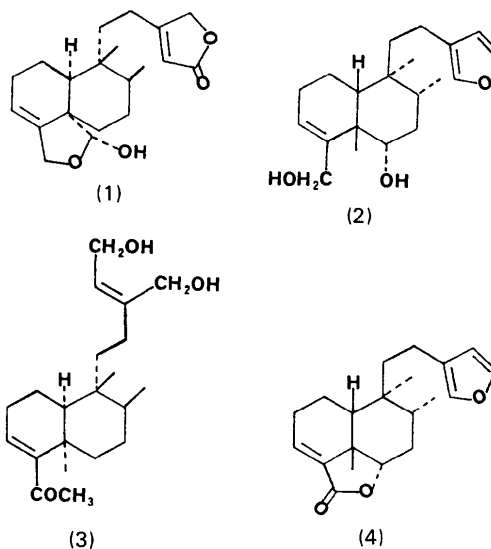
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

(Received 24 February 1986; accepted 8 May 1986)

Abstract. *rel*-(1*R*,6*aS*,7*R*,8*S*,10*S*)-7-[2-(2,5-Dihydro-5-oxo-3-furanyl)ethyl]-3,5,6,6*a*,7,8,9,10-octahydro-1-hydroxy-7,8-dimethyl-1*H*-naphtho[1,8*a*-c]furan, C₂₀H₂₈O₄, *M_r* = 332.44, orthorhombic, *P*2₁2₁2₁, *a* = 9.643 (1), *b* = 23.114 (9), *c* = 8.008 (1) Å, *V* = 1784.9 (8) Å³, *Z* = 4, *D_x* = 1.237, *D_m*(flotation) = 1.230 g cm⁻³, λ(Cu *Kα*) = 1.54178 Å, μ = 6.434 cm⁻¹, *F*(000) = 720, *T* = 295 K, *R* = 0.051 for 1316 independent reflections. The title compound is the hemiacetal of the diterpene 18-hydroxy-*cis*-cleroda-3,13(14)-dien-19-*al*-15,16-olide. One six-membered ring exhibits a slightly distorted chair conformation while the other is intermediate between half-chair and 1,2-diplanar. The five-membered hemiacetal ring is in a half-chair conformation while the five-membered lactone ring is almost planar.

Introduction. A detailed knowledge of the secondary metabolite composition is useful in establishing relationships between genera and between species within a genus. The classes of terpenoids, their substitution patterns and particularly their stereochemistry are quite useful in these systematic investigations. *Guitierrezia texana* (Compositae), collected in Texas, yielded ten new *cis*-clerodane-type diterpene lactones (Gao & Mabry, 1986). The majority of clerodane-type diterpenes involve *trans*-fusion of the six-membered rings. The *cis*-fusion of the title compound (1) was inferred from NMR data, and the structure was correlated with compound (2). While the NMR coupling patterns of (1)

and (2) were similar they exhibited opposite optical rotations which implied opposite stereochemistries. The *cis*-fused relative stereochemistry of the ten new *cis*-clerodanes was confirmed by an X-ray diffraction investigation of (1).



Experimental. A clear, colorless prismatic crystal 0.35 × 0.34 × 0.22 mm; density by flotation method using aqueous CsCl solution; Syntex *P*₂₁ diffractometer; θ:2θ scan, variable scan rate; all accessible independent reflections collected within range 7.6 ≤

* To whom correspondence should be addressed.

$2\theta \leq 114.5^\circ$; graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from least-squares refinement of 15 reflections ($29.5 \leq 2\theta \leq 71.2^\circ$) with angles measured by a centering routine associated with diffractometer system; systematic absences ($h00$; $0k0$; $00l$; $h, k, \text{ or } l = 2n + l$) consistent with space group $P2_12_12_1$, Laue symmetry 222; one monitored reflection (051) showed no change in intensity greater than $2\sigma(I)$; 1429 independent reflections measured ($0 \leq h \leq 10$; $0 \leq k \leq 24$, $0 \leq l \leq 8$), 1316 intensities greater than $3\sigma(I)$; 48 sets of equivalent reflections averaged ($R_{\text{int}} = 0.015$); Lorentz and polarization corrections applied, no absorption correction; direct methods (MULTAN78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located all non-H atoms; least-squares refinement followed by difference Fourier synthesis led to location of all H atoms; H-atom parameters refined isotropically but held fixed during final cycles of anisotropic refinement; full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$ [derived from counting statistics evaluated by Syntex (1976) routine]; 217 parameters refined, final $R = 0.051$, $wR = 0.062$, $S = 3.28$, $(\Delta/\sigma)_{\text{max}} = 0.062$, $(\Delta/\sigma)_{\text{avg}} = 0.015$, highest peak or valley in final difference Fourier map $|0.11| \text{ e } \text{Å}^{-3}$; locally written programs for data reduction, ORTEPII (Johnson, 1971), MULTAN78 for direct-methods calculations and XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) for all others; atomic scattering factors for C and O from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965), anomalous-dispersion correction for O scattering factor (International Tables for X-ray Crystallography, 1974) applied. Table 1 lists atomic positional parameters and U_{eq} values while Table 2 lists selected interatomic distances, valence angles and torsion angles.*

Discussion. Fig. 1 is an ORTEP drawing (Johnson, 1971) of the title compound. The two six-membered rings are *cis*-fused which confirms the NMR assignment (Gao & Mabry, 1986). The cyclohexane ring exists as a slightly distorted chair conformation while the cyclohexene ring is distorted by fusion to the five-membered hemiacetal ring. The torsion angles indicate the conformation to be intermediate between 1,2-diplanar and half-chair (Toromanoff, 1980). The *cis*-fusion leads to a sharp folding of the two six-membered rings creating a basket-like cavity. The five-membered hemiacetal ring is in a half-chair conformation with significant strain imparted by the C(5) fusion point, C(4)C(5)C(19)

= $97.7(3)^\circ$. The five-membered lactone ring with torsion angles of $-5.2(5)$ to $5.7(5)^\circ$ is almost planar.

Table 1. Fractional atomic coordinates ($\times 10^4$) for non-H atoms and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

$$U_{\text{eq}} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}cb^*c^*\cos\alpha]$$

	x	y	z	U_{eq}
C(1)	5426 (4)	9144 (2)	13202 (4)	57 (2)
C(2)	6465 (5)	8806 (2)	14236 (5)	73 (3)
C(3)	7700 (5)	8629 (2)	13309 (6)	70 (3)
C(4)	7811 (4)	8703 (2)	11689 (5)	58 (3)
C(5)	6690 (3)	8931 (1)	10547 (4)	42 (2)
C(6)	7058 (4)	9543 (2)	9981 (5)	57 (2)
C(7)	5951 (5)	9820 (2)	8885 (5)	65 (2)
C(8)	4559 (5)	9844 (2)	9739 (6)	67 (3)
C(9)	4091 (4)	9234 (2)	10401 (5)	54 (2)
C(10)	5261 (4)	8920 (1)	11395 (4)	39 (2)
C(11)	3673 (4)	8887 (2)	8806 (5)	51 (2)
C(12)	2978 (4)	8294 (2)	9052 (5)	63 (2)
C(13)	2470 (4)	8077 (2)	7381 (5)	51 (2)
C(14)	3150 (6)	8002 (3)	5989 (6)	108 (4)
C(15)	2208 (6)	7812 (2)	4686 (5)	76 (3)
O(15)	2423 (5)	7711 (2)	3226 (4)	117 (3)
C(16)	1054 (4)	7882 (2)	7108 (5)	78 (3)
O(16)	981 (3)	7729 (1)	5361 (4)	78 (2)
C(17)	4540 (6)	10357 (2)	11000 (8)	93 (4)
C(18)	8981 (4)	8490 (2)	10607 (8)	94 (4)
O(18)	8424 (3)	8470 (1)	8961 (5)	87 (2)
C(19)	6951 (4)	8518 (2)	9060 (5)	52 (2)
O(19)	6346 (3)	7977 (1)	9361 (3)	55 (1)
C(20)	2776 (4)	9300 (2)	11452 (6)	79 (3)

Table 2. Selected interatomic distances (Å), valence angles ($^\circ$) and torsion angles ($^\circ$)

C(1)–C(2)	1.516 (6)	C(9)–C(11)	1.561 (6)
C(1)–C(10)	1.545 (5)	C(9)–C(20)	1.529 (6)
C(2)–C(3)	1.461 (7)	C(11)–C(12)	1.537 (6)
C(3)–C(4)	1.313 (6)	C(12)–C(13)	1.511 (6)
C(4)–C(5)	1.511 (5)	C(13)–C(14)	1.305 (6)
C(4)–C(18)	1.505 (7)	C(13)–C(16)	1.455 (6)
C(5)–C(6)	1.527 (5)	C(14)–C(15)	1.452 (7)
C(5)–C(10)	1.536 (5)	C(15)–O(15)	1.210 (5)
C(5)–C(19)	1.547 (5)	C(15)–O(16)	1.315 (6)
C(6)–C(7)	1.523 (6)	C(16)–O(16)	1.444 (5)
C(7)–C(8)	1.508 (7)	C(18)–O(18)	1.425 (7)
C(8)–C(9)	1.573 (6)	C(19)–O(18)	1.426 (5)
C(8)–C(17)	1.558 (7)	C(19)–O(19)	1.400 (5)
C(9)–C(10)	1.560 (5)		
C(2)C(1)C(10)	114.0 (3)	C(8)C(9)C(10)	112.4 (3)
C(1)C(2)C(3)	113.9 (4)	C(1)C(10)C(5)	108.4 (3)
C(2)C(3)C(4)	122.1 (4)	C(5)C(10)C(9)	114.5 (3)
C(3)C(4)C(5)	125.8 (4)	C(14)C(13)C(16)	107.6 (4)
C(5)C(4)C(18)	107.6 (4)	C(13)C(14)C(15)	109.9 (4)
C(4)C(5)C(10)	111.6 (3)	C(14)C(15)O(16)	108.1 (4)
C(4)C(5)C(19)	97.7 (3)	C(13)C(16)O(16)	105.5 (3)
C(6)C(5)C(10)	110.8 (3)	C(15)O(16)C(16)	108.6 (3)
C(5)C(6)C(7)	113.4 (3)	C(4)C(18)O(18)	105.1 (3)
C(6)C(7)C(8)	112.2 (3)	C(18)O(18)C(19)	108.7 (3)
C(7)C(8)C(9)	112.0 (3)	C(5)C(19)O(18)	104.7 (3)
C(1)C(2)C(3)C(4)	–7.2 (6)	C(5)C(6)C(7)C(8)	–57.4 (4)
C(2)C(3)C(4)C(5)	–4.7 (7)	C(6)C(7)C(8)C(9)	–53.3 (5)
C(3)C(4)C(5)C(10)	–15.2 (5)	C(7)C(8)C(9)C(10)	48.0 (5)
C(4)C(5)C(10)C(1)	43.5 (4)	C(8)C(9)C(10)C(5)	–46.4 (5)
C(5)C(10)C(1)C(2)	–57.1 (4)	C(9)C(10)C(5)C(6)	48.6 (5)
C(10)C(1)C(2)C(3)	38.9 (4)	C(10)C(5)C(6)C(7)	–53.7 (5)

* Lists of structure factors, H-atom parameters, distances, angles and selected torsion angles, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43041 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

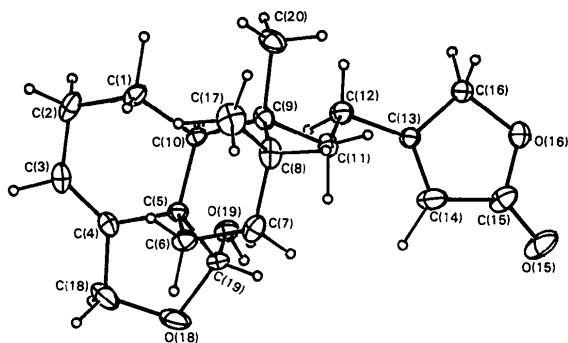


Fig. 1. ORTEP drawing of the title compound. Thermal ellipsoids are drawn at the 35% probability level and H atoms as spheres of arbitrary size.

The NMR of (1) was correlated with that of (2); however, the optical rotation was of opposite sign and the configuration shown in Fig. 1 was inferred (Gao & Mabry, 1986). The crystal structures of the *cis*-clerodanes (3) (Bally, Billet, Durgeat & Heitz, 1976) and (4) (Ferguson, Marsh, McCrindle & Nakamura, 1975; Ferguson & Marsh, 1976) have been reported. The angle between the mean planes of the two six-membered rings ranges between 54 and 65° for compounds (1), (3) and (4). Statistically significant differences in angles and distances in the three compounds are associated with variations in fusion of C(5) and C(6). Methyl C(17) lies within 2.999 (7) Å of methyl C(20) and within 3.178 (7) Å of C(6) with a C(17)C(8)C(9)C(20) torsion angle of 44.6 (5)°. There is an intermolecular H bond formed between OH(19)

and O(15) (0.5 + *x*, 1.5 - *y*, 1 - *z*), O(19)···O(15) = 2.811 (4) Å, H(19)···O(15) = 1.83 (4) Å and O(19)–H(19)···O(15) = 164 (1)°.

We thank the Welch Foundation (P-074) and NSF (INT8214877) for financial support.

References

- BALLEY, R., BILLET, D., DURGEAT, M. & HEITZ, S. (1976). *Tetrahedron Lett.* pp. 2777–2778.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst. A* **24**, 321–324.
 FERGUSON, G. & MARSH, W. C. (1976). *Cryst. Struct. Commun.* **5**, 35–38.
 FERGUSON, G., MARSH, W. C., MCCRINDLE, R. & NAKAMURA, E. (1975). *J. Chem. Soc. Chem. Commun.* p. 299.
 GAO, F. & MABRY, T. J. (1986). *Phytochemistry*. In the press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press (Present distributor D. Reidel, Dordrecht.)
 JOHNSON, C. K. (1971). ORTEPII. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 Syntex (1976). *XTL/XTLE Structure Determination System*. Syntex Analytical Instruments, Cupertino, California.
 TOROMANOFF, E. (1980). *Tetrahedron*, **36**, 2809–2931.

Acta Cryst. (1986). **C42**, 1442–1444

Structure of Methyl(1,5,6-trihydroxy-1,2,3,4-tetrahydro-2-naphthyl)ammonium Bromide

BY TREVOR W. HAMBLEY* AND JOHN R. RODGERS

Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, Australia 5001

(Received 20 February 1986; accepted 9 May 1986)

Abstract. C₁₁H₁₆NO₃⁺.Br⁻, *M_r* = 290.2, triclinic, *P* $\bar{1}$, *a* = 7.710 (5), *b* = 8.762 (8), *c* = 9.882 (2) Å, α = 104.15 (2), β = 106.19 (4), γ = 95.66 (7)°, *V* = 611.6 Å³, *Z* = 2, *D_m* = 1.56 (2), *D_x* = 1.575 g cm⁻³, Mo *K*α, λ = 0.71069 Å, μ = 32.6 cm⁻¹, *F*(000) = 296, *T* = 294 K, final *R* = 0.051 for 1440 reflections. The cyclohexane moiety adopts a half-chair conformation with the hydroxyl and protonated amine groups in

diequatorial orientations. The O–C(1)–C(2)–N(1) and C(9)–C(1)–C(2)–N(1) torsion angles are 63 (1) and 172 (1)°, respectively.

Introduction. The determination of the active conformations of hormones and drugs is important since such information can be used to infer molecular modes of action and in the design of new drugs. However, many active molecules are very flexible and while solid-state and isolated-state geometries can be obtained by crystallographic and theoretical methods,

* Present address: Department of Inorganic Chemistry, University of Sydney, Sydney 2006, Australia.