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Haplociliatic Acid, $C_{20}H_{32}O_4$

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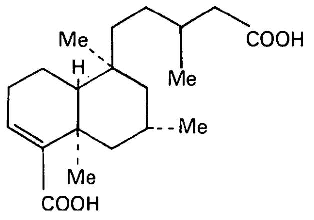
Abstract. $M_r = 336{\cdot}47$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}946$ (3), $b = 14{\cdot}408$ (3), $c = 10{\cdot}254$ (2) Å, $V = 1912{\cdot}7$ (7) Å^3, $Z = 4$, $D_m = 1{\cdot}16$, $D_x = 1{\cdot}168$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 6{\cdot}4$ cm^{-1}, $F(000) = 736$, $T = 298$ K, $R = 0{\cdot}059$ for 1959 reflections. Haplociliatic acid is a *trans*-clerodane type of diterpene diacid containing two *trans*-fused six-membered rings. The two rings exhibit sofa and chair conformations with one acid function in conjugation with a double bond of the six-membered ring. Both acid functions are involved in intermolecular hydrogen bonding.

Introduction. Haplociliatic acid (1) is a dihydro-*trans*-clerodane-type diterpene diacid isolated from *Haplopapus ciliatus* (Nutt.) DC (Bittner, Zabel, Smith & Watson, 1978). It is a stereoisomer of cistodoic acid (Berti, Livi & Segnini, 1970; Anderson, McCrindle & Nakamura, 1974), a *cis*-clerodane diterpene.



(1)

Experimental. Crystal (1) 0·7 × 0·8 × 0·9 mm, D_m by flotation, Syntex $P2_1$, θ:2θ scan, variable scan speed, graphite monochromator, Cu $K\alpha$ radiation, room-temperature lattice parameters by least-squares refinement of 15 reflections whose angles were measured by a centering routine associated with the Syntex diffractometer, systematic absences ($h = 2n + 1$ for $h00$, $k = 2n + 1$ for $0k0$, $l = 2n + 1$ for $00l$) consistent with space group $P2_12_12_1$; a periodically monitored reflection showed no significant change in intensity; 2011 independent reflections measured ($2\theta \leq 140°$; $h \leq 15$, $k \leq 17$, $l \leq 12$), 48 with intensities less than $2\sigma(I)$ (not used in the refinement); four additional reflections showed significant secondary extinction and were omitted from the refinement; Lorentz and polarization corrections, no absorption; direct methods, *MULTAN* (Germain, Main & Woolfson, 1971) revealed positions of all nonhydrogen atoms; after several cycles of least-squares refinement H atoms were located in a difference Fourier map; full-matrix least-squares refinement, anisotropic for nonhydrogen atoms, led to $R = 0{\cdot}059$, $R_w = 0{\cdot}061$, $S = 3{\cdot}25$; $\sum\omega(|F_o| - |F_c|)^2$ minimized, $\omega = 1/\sigma^2(F_o)$ determined from counting statistics, H atoms isotropic; final difference map showed no peak larger than 0·2 e Å^{-3}, average and maximum shift/error 0·21 and 0·84; Hamilton (1965) significance test indicates the absolute configuration can be accepted at the 90% significance level; atomic scattering factors and corrections for the real and imaginary portions of the anomalous dispersion were calculated by XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), locally written programs were used for data reduction and initial least-squares refinement, *MULTAN*78 for direct-methods calculations and XRAY76 for all others.‡

Discussion. Table 1 gives a list of atomic positional parameters while Table 2 lists interatomic distances, valence angles and torsion angles.

Table 1. *Positional parameters* (× 10^4, *for* H × 10^3) *and thermal parameters*

	x	y	z	B_{eq}/B^* (Å^2)
C(1)	6911 (2)	6332 (1)	6387 (3)	5·0
C(2)	5936 (2)	5989 (2)	7063 (3)	5·8
C(3)	5478 (2)	6737 (2)	7891 (3)	5·5
C(4)	5765 (2)	7623 (2)	7893 (2)	5·0
C(5)	6582 (1)	8009 (1)	6956 (2)	4·6
C(6)	6191 (2)	8916 (1)	6325 (3)	5·1
C(7)	6884 (2)	9244 (1)	5221 (3)	5·4
C(8)	7035 (2)	8517 (2)	4145 (3)	5·2
C(9)	7452 (2)	7594 (1)	4702 (2)	4·6
C(10)	6723 (1)	7296 (1)	5828 (2)	4·2
C(11)	7444 (2)	6844 (2)	3622 (3)	5·1
C(12)	6405 (2)	6509 (2)	3111 (3)	5·4
C(13)	6532 (2)	5769 (2)	2041 (2)	5·2
C(14)	5536 (2)	5221 (2)	1820 (3)	6·1
C(15)	5284 (2)	4655 (2)	3006 (3)	5·7
C(16)	6900 (4)	6192 (3)	763 (3)	8·0
C(17)	7678 (3)	8937 (2)	3050 (4)	7·4
C(18)	7568 (2)	8188 (2)	7778 (3)	5·8
C(19)	5347 (2)	8229 (2)	8938 (3)	5·7
C(20)	8604 (2)	7666 (2)	5098 (3)	5·5

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‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38481 (15 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 (*cont.*)

	x	y	z	B_{eq}/B^*(Å^2)
O(21)	5772 (2)	3974 (2)	3302 (3)	10·1
O(22)	4504 (2)	4961 (2)	3695 (3)	7·9
O(23)	5698 (2)	9009 (2)	9170 (3)	8·1
O(24)	4589 (2)	7880 (2)	9630 (3)	9·3
H(1*a*)	761 (3)	617 (3)	700 (4)	7·7 (10)
H(1*b*)	711 (2)	593 (2)	571 (3)	5·4 (7)
H(2*a*)	534 (2)	582 (2)	645 (2)	3·0 (4)
H(2*b*)	597 (2)	538 (3)	764 (4)	6·5 (8)
H(3)	505 (3)	660 (3)	843 (5)	8·1 (11)
H(6*a*)	607 (3)	941 (3)	698 (4)	7·4 (10)
H(6*b*)	549 (2)	870 (2)	605 (3)	5·3 (8)
H(7*a*)	774 (2)	927 (2)	553 (3)	4·2 (6)
H(7*b*)	672 (6)	988 (6)	482 (11)	16·0 (28)
H(8)	625 (3)	829 (3)	376 (4)	7·3 (10)
H(10)	606 (3)	716 (3)	529 (4)	7·6 (11)
H(11*a*)	794 (3)	712 (3)	280 (5)	9·7 (12)
H(11*b*)	782 (2)	624 (2)	384 (3)	3·8 (5)
H(12*a*)	610 (2)	701 (3)	274 (3)	5·1 (7)
H(12*b*)	600 (4)	607 (4)	382 (6)	9·4 (14)
H(13)	713 (2)	524 (2)	229 (4)	5·9 (8)
H(14*a*)	555 (3)	495 (3)	104 (6)	8·8 (12)
H(14*b*)	500 (2)	578 (3)	161 (4)	6·3 (9)
H(16*a*)	721 (3)	561 (4)	24 (5)	8·8 (12)
H(16*b*)	746 (4)	668 (4)	81 (5)	9·2 (14)
H(16*c*)	655 (8)	656 (8)	38 (11)	17·0 (34)
H(17*a*)	793 (3)	857 (3)	216 (4)	6·9 (9)
H(17*b*)	729 (3)	960 (3)	275 (4)	7·3 (9)
H(17*c*)	840 (4)	905 (3)	328 (6)	9·6 (13)
H(18*a*)	729 (5)	830 (5)	866 (8)	12·1 (17)
H(18*b*)	796 (3)	770 (3)	780 (5)	8·2 (12)
H(18*c*)	799 (4)	861 (4)	746 (6)	10·9 (17)
H(20*a*)	904 (3)	763 (2)	444 (3)	5·3 (7)
H(20*b*)	874 (2)	723 (2)	568 (3)	3·7 (6)
H(20*c*)	872 (5)	835 (5)	549 (7)	11·7 (24)
H(22)	428 (5)	465 (6)	442 (8)	12·9 (18)
H(24)	451 (4)	832 (4)	1044 (5)	8·7 (14)

* $B_{eq} = 8\pi^2(U_1U_2U_3)^{1/3}$.

Table 2. *Interatomic distances* (Å), *valence angles* (°), *and torsion angles*(°)

C(1)—C(2)	1·522 (4)	C(9)—C(10)	1·551 (3)
C(1)—C(10)	1·522 (3)	C(9)—C(11)	1·548 (3)
C(2)—C(3)	1·495 (4)	C(9)—C(20)	1·550 (3)
C(3)—C(4)	1·329 (3)	C(11)—C(12)	1·522 (3)
C(4)—C(5)	1·534 (3)	C(12)—C(13)	1·540 (3)
C(4)—C(19)	1·485 (3)	C(13)—C(14)	1·528 (4)
C(5)—C(6)	1·544 (3)	C(13)—C(16)	1·522 (4)
C(5)—C(10)	1·558 (3)	C(14)—C(15)	1·501 (4)
C(5)—C(18)	1·550 (3)	C(15)—O(21)	1·205 (4)
C(6)—C(7)	1·519 (4)	C(15)—O(22)	1·309 (3)
C(7)—C(8)	1·534 (4)	C(19)—O(23)	1·235 (3)
C(8)—C(9)	1·544 (3)	C(19)—O(24)	1·311 (4)
C(8)—C(17)	1·523 (4)		
C(1)—H(1*a*)	1·13 (4)	C(13)—H(13)	1·11 (3)
C(1)—H(1*b*)	0·94 (3)	C(14)—H(14*a*)	0·89 (6)
C(2)—H(2*a*)	1·02 (2)	C(14)—H(14*b*)	1·09 (4)
C(2)—H(2*b*)	1·07 (4)	C(16)—H(16*a*)	1·07 (5)
C(3)—H(3)	0·81 (5)	C(16)—H(16*b*)	1·02 (5)
C(6)—H(6*a*)	0·99 (4)	C(16)—H(16*c*)	0·79 (11)
C(6)—H(6*b*)	1·00 (3)	C(17)—H(17*a*)	1·10 (4)
C(7)—H(7*a*)	1·16 (2)	C(17)—H(17*b*)	1·12 (4)
C(7)—H(7*b*)	1·03 (9)	C(17)—H(17*c*)	0·98 (6)
C(8)—H(8)	1·14 (4)	C(18)—H(18*a*)	0·99 (8)
C(10)—H(10)	1·04 (4)	C(18)—H(18*b*)	0·87 (5)
C(11)—H(11*a*)	1·13 (5)	C(18)—H(18*c*)	0·88 (6)
C(11)—H(11*b*)	1·02 (3)	C(20)—H(20*a*)	0·88 (3)
C(12)—H(12*a*)	0·90 (3)	C(20)—H(20*b*)	0·88 (3)
C(12)—H(12*b*)	1·10 (6)	C(20)—H(20*c*)	1·08 (7)
O(22)—H(22)	0·92 (8)	O(24)—H(24)	1·05 (5)
C(2)C(1)C(10)	108·6 (2)	C(8)C(9)C(11)	109·6 (2)
C(1)C(2)C(3)	110·7 (2)	C(8)C(9)C(20)	112·1 (2)
C(2)C(3)C(4)	125·6 (2)	C(10)C(9)C(11)	109·6 (2)
C(3)C(4)C(5)	122·7 (2)	C(10)C(9)C(20)	114·1 (2)
C(3)C(4)C(19)	117·7 (2)	C(11)C(9)C(20)	103·9 (2)
C(5)C(4)C(19)	119·3 (2)	C(1)C(10)C(5)	109·9 (2)
C(4)C(5)C(6)	110·1 (2)	C(1)C(10)C(9)	115·8 (2)
C(4)C(5)C(10)	107·8 (2)	C(5)C(10)C(9)	116·2 (2)
C(4)C(5)C(18)	106·7 (2)	C(9)C(11)C(12)	118·2 (2)
C(6)C(5)C(10)	106·5 (2)	C(11)C(12)C(13)	111·7 (2)
C(6)C(5)C(18)	110·9 (2)	C(12)C(13)C(14)	111·9 (2)
C(10)C(5)C(18)	114·7 (2)	C(12)C(13)C(16)	111·7 (2)
C(5)C(6)C(7)	112·4 (2)	C(14)C(13)C(16)	110·0 (2)
C(6)C(7)C(8)	113·5 (2)	C(13)C(14)C(15)	110·1 (2)
C(7)C(8)C(9)	111·5 (2)	C(14)C(15)O(21)	122·2 (3)
C(7)C(8)C(17)	109·2 (2)	C(14)C(15)O(22)	114·9 (2)
C(9)C(8)C(17)	115·1 (2)	O(21)C(15)O(22)	122·9 (3)
C(8)C(9)C(10)	107·5 (2)	C(4)C(19)O(24)	116·0 (2)
C(4)C(19)O(23)	122·7 (2)	O(23)C(19)O(24)	121·4 (3)
1—2—3—4	10·1 (4)	5—6—7—8	56·3 (3)
2—3—4—5	4·0 (4)	6—7—8—9	−55·5 (2)
3—4—5—10	16·7 (3)	7—8—9—10	53·0 (2)
4—5—10—1	−51·2 (2)	8—9—10—5	−57·0 (2)
5—10—1—2	67·8 (2)	9—10—5—6	56·7 (2)
10—1—2—3	−44·8 (3)	10—5—6—7	−53·6 (2)
3—4—19—24	−11·7 (3)	9—11—12—13	179·8 (2)
3—4—19—23	166·8 (3)	11—12—13—14	162·5 (4)
5—4—19—23	−7·1 (3)	12—13—14—15	−66·1 (3)
5—4—19—24	174·3 (4)	12—11—9—20	172·9 (3)

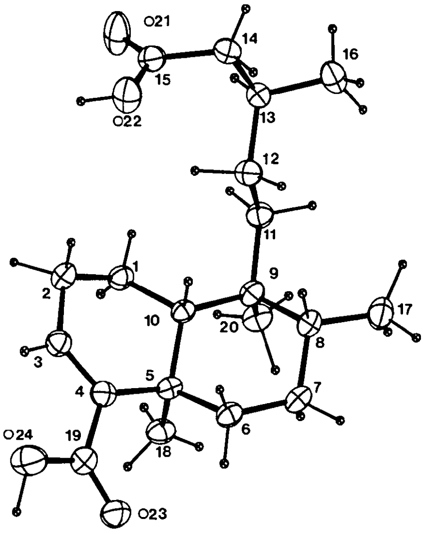

Fig. 1. *ORTEP* drawing of haplociliatic acid. Thermal ellipsoids are drawn at the 35% probability level while hydrogen atoms are represented by spheres of arbitrary radius.

Fig. 1 is an *ORTEP* drawing (Johnson, 1965) of haplociliatic acid. The two six-membered rings exhibit sofa and chair conformations. The acid side chain at C(4) is conjugated with the C(3)—C(4) double bond as indicated by the shortening of C(4)—C(19) to 1·485 (3) Å and the lengthening of C(19)—O(23) to 1·235 (3) Å; however, the system is twisted slightly from coplanarity as indicated by torsion angles C(3)C(4)C(19)O(24) = −11·7 (4) and C(3)C(4)C(19) O(23) = 166·8 (3)°. The bond distances may be compared with those of the side-chain acid function where C(14)—C(15) = 1·501 (4) and C(15)—O(21) = 1·205 (4) Å. The C(18) and C(17) methyl groups occupy axial sites with a C(18)···C(20) distance of 3·149 (4) Å while the C(17) methyl and C(9) side chain are equatorial. Atoms C(9), C(11), C(12) and C(13) are extended and coplanar while the remainder of the side chain is twisted back toward the six-membered rings. The two acid functions are involved in hydrogen bonding with O(22)—H(22) = 0·92 (8), O(22)$\cdots$O(23) $(1-x,\ 0\cdot5+y,\ 1\cdot5-z)$ = 2·597 (4), H(22)$\cdots$O(23) = 1·72 (9) Å, $\angle$O(22)—H(22)$\cdots$O(23) = 160·5 (5)°; and O(24)—H(24) = 1·05 (5), O(24)$\cdots$O(21) $(1-x,\ 0\cdot5+y,\ 1\cdot5-z)$ = 2·683 (4), H(24)$\cdots$O(21) = 1·64 (5) Å, O(24)—H(24)$\cdots$O(21) = 172·6 (5)°. Haplociliatic acid is the C(10) epimer of the *cis*-clerodane cistodoic acid (Berti, Livi & Segnini, 1970).

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Structure of 3-(*o*-Carboxyphenyl)-1-phenyltriazene 1-Oxide, $C_{13}H_{11}N_3O_3$

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Abstract. $M_r = 257\cdot0$, monoclinic, $P2_1/n$, $a = 8\cdot006\ (3)$, $b = 11\cdot523\ (6)$, $c = 13\cdot937\ (10)$ Å, $\beta = 102\cdot09\ (4)°$, $V = 1257\ (1)$ Å^3, $Z = 4$, $D_m = 1\cdot25$ Mg m^{-3} (aq. KI), $D_x = 1\cdot36$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0\cdot78$ mm^{-1}, $F(000) = 536$, room temperature. Final value of $R = 0\cdot051$ for 1499 reflections. The structure establishes the *N*-oxide form of the triazene and reveals both intramolecular [N(3)—H(5)$\cdots$O(3) = 2·659 (3) Å] and intermolecular [O(1)$\cdots$H(4)—O(2) = 2·643 (2) Å] hydrogen bonds, the latter being responsible for the formation of dimers.

Introduction. This paper is part of a systematic study in progress on the metal complexes of the title compound. The compound is used as an analytical reagent and as a potential ligand for synthesis of complexes. IR studies show that the triazene should exist as the *N*-oxide instead of the *N*-hydroxy form (Majumdar & Saha, 1976). The present investigation confirms the *N*-oxide form.

Experimental. Light-yellow crystals (from ethanol), 0·55 × 0·32 × 0·17 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, least-squares cell parameters from 25 reflections taken from all octants in reciprocal space, scattering factors for non-hydrogen atoms from *International Tables for X-ray crystallography* (1962) and, for H atoms, from Stewart, Davidson & Simpson (1965), 1858 $\pm hkl$ with $2\theta < 50°$, 1499 independent, 359 with $I < 2\sigma(I)$, Lp correction applied, absorption ignored; direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), non-hydrogen atoms anisotropic full-matrix, H atoms (from ΔF synthesis and also calculated from known geometry around C atoms) isotropic: maximum and minimum heights in final difference Fourier map $\pm0\cdot2$e Å^{-3}, maximum least-squares shift-to-error ratio 0·255 and average shift-to-error ratio 0·088, final $R = 0\cdot051$ with 216 parameters and $R_w = 0\cdot078$; block-diagonal approximation [$\sum w(\Delta F)^2$ minimized] used with a weighting factor $w = 1/\sigma^2(F)$, with $\sigma(F) = R_i|F_o|$ (Seal & Ray, 1981); Burroughs 6700 computer (Regional Computer Centre, Calcutta), modified versions of *MAMIE* and *BLOK* from the X-RAY ARC program system.

Discussion. The atomic coordinates are listed in Table 1 and interatomic distances and angles in Table 2.‡ The phenyl rings of the molecule are inclined to one another by 13·3 (1)°. All bond lengths and bond angles agree well with the values reported in the literature. The double-bond distance N(1)—N(2) is shorter than

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‡ Lists of structure factors, anisotropic thermal parameters and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38507 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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