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Plucheinol and (3αH)-Plucheinol

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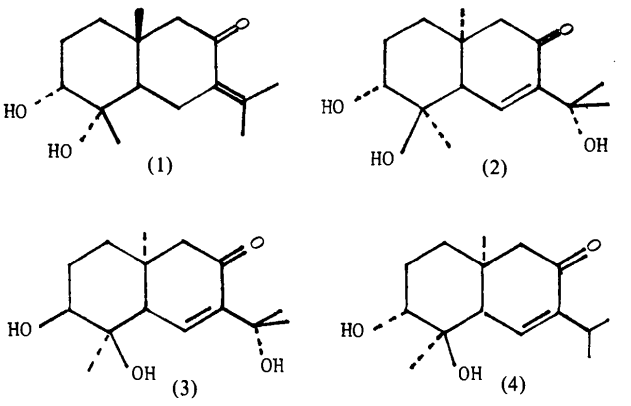
Abstract

Plucheinol, $C_{15}H_{24}O_4.H_2O$, and (3αH)-plucheinol, $C_{15}H_{24}O_4.\frac{1}{2}H_2O$, are eudesmane-type sesquiterpenes isolated from *Pluchea chingoyo*. The compounds crystallize in space groups $P2_12_12_1$ and $P2_1$ with unit-cell dimensions $a = 9{\cdot}902\ (2)$, $b = 24{\cdot}179\ (6)$, $c = 6{\cdot}259\ (2)$ Å and $V = 1498{\cdot}5\ (6)$ Å^3 for plucheinol and $a = 11{\cdot}034\ (2)$, $b = 12{\cdot}143\ (2)$, $c = 11{\cdot}509\ (2)$ Å, $\beta = 95{\cdot}83\ (2)°$ and $V = 1534{\cdot}1\ (4)$ Å^3 for (3αH)-plucheinol. The monoclinic cell of (3αH)-plucheinol contains two independent molecules per asymmetric unit. The structures refined to R factors of 0·058 for 1617 observed reflexions and 0·050 for 2712 observed reflexions, respectively. Both structures contain water of hydration which is involved in a very extensive hydrogen-bond network. The cyclohexane rings exhibit chair conformations while the cyclohexenone rings are found in 1,2-diplanar (puckered sofa) conformations. The two independent (3αH)-plucheinol molecules adopt slightly different conformations because of hydrogen-bond formation.

Introduction

Pluchea (Compositae) is a genus of approximately 40 species distributed throughout the warmer climates of the Americas. *Pluchea* species from Mexico, Central America and Colombia have been used as folk remedies and the most common use has been in the treatment of tumors. *Pluchea odorata* from Mexico was also found to be a plant-growth inhibitor and the active ingredient was identified as the sesquiterpene cuauhtemone (1) (Ivie, Watson & Dominguez, 1974; Nakanishi, Crouch, Miura, Dominguez, Zamudio & Villarreal, 1974). Although *Pluchea chingoyo* from Chile has no history of use as a folk medicine, extracts of the plant give a positive test in the KB cell bioassay. Extracts of *Pluchea chingoyo* yielded the sesquiterpene cuauhtemone and three new compounds named plucheinol (2), (3αH)-plucheinol (3) and pluchein (4). The structures and relative configurations of plucheinol and (3αH)-plucheinol were established by X-ray diffraction studies while the structure of pluchein was assigned from ^{13}C NMR chemical shifts and line multiplicities (Chiang, Bittner, Silva & Watson, 1979). The absolute configuration of cuauhtemone (1) was assigned through use of a differential CD curve before and after addition of $Pr(dpm)_3$ (dpm is dipivaloylmethane) to a CCl_4 solution of the terpene (Nakanishi, Crouch, Miura, Dominguez, Zamudio & Villarreal, 1974). To be consistent plucheinol and (3αH)-plucheinol should be assigned the same absolute configuration; however, Hamilton significance tests (Hamilton, 1965), although not strongly significant (0·70 confidence level), indicate a slight preference for the configurations shown in (2) and (3). The coordinates, torsion angles and figures are consistent with the latter configuration.



Data collection and structure refinement

All intensity data were collected on a Syntex $P2_1$ diffractometer system with the $\theta{:}2\theta$ scanning technique with a variable scan speed and a graphite

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monochromator with Cu $K\alpha$ radiation (λ = 1·54178 Å). Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the diffractometer. Space-group assignments were consistent with systematic absences. Periodically monitored reflexions showed no significant changes in intensity. Lorentz and polarization corrections were applied, but no absorption corrections were made.

Table 1. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *for plucheinol*

	x	y	z	U^*_{eq} or U (Å^2)
C(1)	5449 (2)	6922 (1)	9254 (4)	3·9†
C(2)	6057 (2)	6529 (1)	10866 (4)	3·8
C(3)	5960 (2)	5935 (1)	10110 (4)	3·0
C(4)	4490 (2)	5751 (1)	9660 (3)	2·6
C(5)	3877 (2)	6175 (1)	8101 (3)	2·6
C(6)	2469 (2)	6029 (1)	7374 (3)	2·9
C(7)	1597 (2)	6383 (1)	6519 (3)	2·7
C(8)	2032 (2)	6969 (1)	6228 (4)	3·1
C(9)	3454 (2)	7114 (1)	6856 (4)	3·4
C(10)	3963 (2)	6784 (1)	8781 (3)	2·9
O(11)	6571 (2)	5568 (1)	11631 (3)	4·0
O(12)	4534 (1)	5238 (1)	8496 (2)	3·3
C(13)	3668 (2)	5654 (1)	11687 (4)	3·4
C(14)	173 (2)	6214 (1)	5858 (4)	2·7
O(15)	−22 (2)	5637 (1)	6248 (3)	3·6
C(16)	−45 (2)	6283 (1)	3463 (4)	3·9
C(17)	−878 (3)	6540 (1)	7119 (5)	4·3
O(18)	1280 (2)	7320 (1)	5482 (4)	4·6
C(19)	3091 (2)	6943 (1)	10705 (4)	3·7
O(20)	6085 (2)	4880 (1)	5018 (3)	4·4
H(1*a*)	545 (3)	728 (1)	996 (5)	3·7
H(1*b*)	598 (3)	689 (1)	793 (5)	3·0
H(2*a*)	702 (3)	658 (1)	1124 (5)	2·8
H(2*b*)	553 (4)	655 (1)	1221 (7)	5·2
H(3)	647 (3)	589 (1)	865 (4)	3·4
H(5)	454 (2)	611 (1)	682 (4)	2·3
H(6)	232 (2)	560 (1)	726 (4)	1·7
H(9*a*)	390 (3)	707 (1)	579 (5)	2·3
H(9*b*)	349 (4)	756 (1)	713 (8)	6·3
H(11)	739 (3)	541 (1)	1115 (6)	5·1
H(12)	471 (3)	492 (1)	943 (4)	2·1
H(13*a*)	366 (3)	603 (1)	1273 (6)	3·4
H(13*b*)	285 (4)	559 (1)	1122 (6)	3·8
H(13*c*)	392 (5)	529 (2)	1246 (10)	7·7
H(15)	−32 (5)	557 (2)	722 (10)	6·1
H(16*a*)	−98 (5)	618 (2)	291 (8)	5·6
H(16*b*)	22 (5)	664 (2)	282 (9)	6·5
H(16*c*)	48 (3)	602 (1)	266 (5)	2·9
H(17*a*)	−201 (10)	632 (3)	679 (15)	12·8
H(17*b*)	−81 (4)	646 (2)	879 (8)	5·8
H(17*c*)	−77 (12)	702 (4)	676 (15)	17·0
H(19*a*)	212 (4)	676 (1)	1060 (6)	4·4
H(19*b*)	302 (3)	726 (1)	1068 (6)	3·2
H(19*c*)	342 (3)	677 (1)	1198 (6)	2·6
H(20*a*)	556 (5)	502 (1)	607 (7)	4·8
H(20*b*)	632 (6)	515 (2)	405 (11)	7·9

* $U_{eq} = (U_{11} U_{22} U_{33})^{1/3}$.
† E.s.d.'s are 0·1 Å^2 for all values.

Table 2. *Atomic positional coordinates* ($\times 10^4$, *for* H $\times 10^3$) *for* (3αH)*-plucheinol*

Molecule 1

	x	y	z	U^*_{eq} or U (Å^2)
C(1)	2383 (2)	1166 (2)	3664 (2)	3·8 (1)
C(2)	3250 (2)	1944 (2)	3111 (2)	4·0 (1)
C(3)	3066 (2)	3142 (2)	3452 (2)	3·8 (1)
C(4)	1736 (2)	3533 (2)	3153 (2)	3·3 (1)
C(5)	893 (2)	2706 (2)	3690 (2)	3·0 (1)
C(6)	−419 (2)	3052 (2)	3582 (2)	3·4 (1)
C(7)	−1349 (2)	2367 (2)	3689 (2)	3·5 (1)
C(8)	−1081 (2)	1184 (2)	3910 (2)	3·6 (1)
C(9)	236 (2)	839 (2)	4116 (2)	3·8 (1)
C(10)	1047 (2)	1488 (2)	3354 (2)	3·3 (1)
O(11)	3376 (2)	3236 (2)	4685 (2)	4·4 (1)
O(12)	1590 (2)	4600 (2)	3673 (2)	4·0 (1)
C(13)	1459 (3)	3740 (3)	1849 (2)	4·4 (1)
C(14)	−2681 (2)	2744 (3)	3560 (2)	4·0 (1)
O(15)	−3324 (2)	2267 (2)	4467 (2)	5·0 (1)
C(16)	−2795 (3)	3965 (3)	3735 (4)	5·5 (1)
C(17)	−3288 (3)	2404 (4)	2364 (3)	6·0 (2)
O(18)	−1900 (2)	501 (2)	3957 (2)	4·8 (1)
C(19)	641 (3)	1208 (3)	2070 (2)	4·4 (1)
H_2O(20)	4569 (2)	5089 (2)	5342 (2)	5·0 (1)
H(1*a*)	259 (2)	120 (3)	448 (3)	2·9 (6)
H(1*b*)	251 (3)	47 (3)	342 (3)	3·8 (8)
H(2*a*)	311 (3)	192 (3)	230 (3)	3·2 (7)
H(2*b*)	412 (4)	170 (4)	336 (4)	6·7 (11)
H(3)	358 (3)	363 (3)	300 (3)	4·1 (8)
H(5)	119 (3)	275 (3)	452 (3)	4·5 (8)
H(6)	−61 (4)	383 (4)	342 (4)	5·8 (11)
H(9*a*)	30 (4)	8 (4)	384 (4)	6·0 (10)
H(9*b*)	48 (2)	102 (3)	495 (3)	3·0 (6)
H(11)	368 (4)	379 (5)	475 (4)	6·5 (13)
H(12)	182 (4)	465 (5)	434 (5)	7·3 (14)
H(13*a*)	166 (3)	306 (3)	141 (3)	4·4 (8)
H(13*b*)	58 (4)	399 (5)	157 (4)	7·4 (13)
H(13*c*)	191 (5)	446 (5)	159 (4)	8·4 (14)
H(15)	−323 (5)	161 (6)	425 (5)	7·9 (16)
H(16*a*)	−248 (4)	430 (4)	302 (4)	6·0 (11)
H(16*b*)	−230 (4)	417 (4)	452 (4)	7·3 (12)
H(16*c*)	−369 (3)	414 (4)	366 (3)	5·7 (10)
H(17*a*)	−329 (4)	167 (5)	220 (4)	6·1 (12)
H(17*b*)	−279 (4)	282 (5)	176 (4)	7·3 (12)
H(17*c*)	−409 (4)	264 (5)	235 (4)	7·3 (12)
H(19*a*)	116 (4)	144 (4)	148 (4)	7·0 (12)
H(19*b*)	−10 (4)	148 (4)	182 (4)	6·2 (11)
H(19*c*)	63 (4)	44 (4)	193 (3)	5·4 (10)
H(20*a*)	517 (5)	460 (5)	575 (5)	8·4 (14)
H(20*b*)	491 (5)	562 (5)	480 (4)	7·5 (13)

Molecule 2

C(1)	4833 (3)	9062 (4)	1309 (3)	5·7
C(2)	3763 (3)	8333 (4)	1512 (3)	5·6
C(3)	3987 (2)	7650 (3)	2627 (3)	4·6
C(4)	5180 (2)	6973 (3)	2689 (2)	3·8
C(5)	6235 (2)	7732 (2)	2396 (2)	3·6
C(6)	7451 (2)	7160 (2)	2514 (2)	3·7
C(7)	8439 (2)	7536 (2)	2059 (2)	3·8
C(8)	8338 (2)	8588 (3)	1387 (2)	4·1
C(9)	7119 (3)	9180 (3)	1301 (3)	4·9
C(10)	6021 (2)	8399 (3)	1259 (2)	4·2
O(11)	4002 (2)	8380 (2)	3592 (2)	5·1

Table 2 (*cont.*)

	x	*y*	*z*	U^*_{eq} or U (Å²)
O(12)	5472 (2)	6582 (2)	3856 (2)	4·2
C(13)	4987 (3)	5942 (3)	1938 (3)	5·3
C(14)	9667 (2)	6964 (2)	2237 (2)	4·0
O(15)	9466 (2)	5957 (2)	2856 (2)	5·0
C(16)	10159 (4)	6667 (4)	1092 (3)	6·8
C(17)	10579 (3)	7666 (4)	3002 (3)	5·2
O(18)	9190 (2)	8995 (2)	950 (2)	5·8
C(19)	5971 (3)	7734 (4)	126 (3)	5·2
H(1*a*)	501 (4)	954 (4)	202 (4)	6·1 (11)
H(1*b*)	464 (4)	948 (4)	58 (4)	6·3 (10)
H(2*a*)	363 (5)	779 (5)	98 (5)	7·6 (14)
H(2*b*)	300 (4)	867 (4)	162 (4)	6·2 (11)
H(3)	329 (3)	710 (3)	260 (2)	3·1 (7)
H(5)	631 (3)	832 (3)	305 (3)	4·6 (8)
H(6)	754 (3)	650 (3)	297 (3)	3·7 (8)
H(9*a*)	703 (4)	965 (4)	57 (4)	6·6 (11)
H(9*b*)	701 (4)	969 (4)	199 (4)	5·6 (9)
H(11)	384 (5)	803 (5)	429 (5)	9·6 (16)
H(12)	565 (4)	711 (5)	418 (4)	5·8 (12)
H(13*a*)	454 (5)	549 (5)	247 (5)	8·2 (14)
H(13*b*)	460 (4)	612 (4)	107 (4)	6·7 (11)
H(13*c*)	577 (4)	565 (4)	185 (4)	6·4 (11)
H(15)	999 (4)	568 (5)	298 (4)	6·1 (13)
H(16*a*)	961 (5)	609 (6)	70 (5)	9·4 (17)
H(16*b*)	1021 (5)	737 (6)	62 (5)	10·1 (18)
H(16*c*)	1098 (4)	629 (5)	130 (4)	8·0 (14)
H(17*a*)	1133 (4)	717 (4)	329 (4)	6·6 (12)
H(17*b*)	1087 (3)	826 (4)	268 (3)	4·9 (9)
H(17*c*)	1024 (4)	786 (5)	369 (5)	7·8 (14)
H(19*a*)	602 (5)	821 (6)	−57 (5)	8·8 (15)
H(19*b*)	664 (6)	716 (7)	−1 (5)	10·2 (18)
H(19*c*)	522 (5)	728 (6)	−4 (5)	8·8 (15)

* $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

Plucheinol (2). $C_{15}H_{24}O_4.H_2O$, M_r = 286·36. Crystal dimensions 0·65 × 0·50 × 0·85 mm. Orthorhombic, $P2_12_12_1$, a = 9·902 (2), b = 24·179 (6), c = 6·259 (2) Å, V = 1498·5 (6) Å³, Z = 4, d_c = 1·269 Mg m⁻³. Of the 1638 independent reflexions measured, 12 had intensities less than $2\sigma(I)$ and were not used in the refinement. Nine additional reflexions were omitted because of secondary extinction.

(3αH)-*Plucheinol* (3). $C_{15}H_{24}O_4.\frac{1}{2}H_2O$, M_r = 277·36. Crystal dimensions 0·3 × 0·2 × 0·2 mm. Monoclinic, $P2_1$, a = 11·034 (2), b = 12·143 (2), c = 11·509 (2) Å, β = 95·83 (2)°, V = 1534·1 (4) Å³, Z = 4, d_c = 1·199 Mg m⁻³. Of the 3021 independent reflexions measured, 305 had intensities less than $2\sigma(I)$ and were not included in the refinement. Four additional reflexions were omitted because of secondary extinction.

The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 400 $|E|$ values greater than 1·16 for the plucheinol data. The phase set with the largest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of all nonhydrogen atoms. Least-squares refinement was terminated at R = 0·058 where $R = \sum||F_o| - |F_c||/\sum|F_o|$. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(I)$ was determined from counting statistics. H-atom thermal parameters were refined isotropically.

The structure of (3αH)-plucheinol could not be solved with *MULTAN* although numerous manually selected starting sets were tried. The structure was solved with *QTAN* (Langs & De Titta, 1975) and the first E map revealed the positions of 36 of the 39 heavy atoms in the asymmetric unit. The remaining heavy atoms and most of the hydrogen atoms were located by

Table 3. *Interatomic distances* (Å)

		(3αH)-Plucheinol	
	Plucheinol	Molecule 1	Molecule 2
C(1)–C(2)	1·512 (3)	1·529 (4)	1·513 (5)
C(1)–C(10)	1·537 (3)	1·532 (3)	1·544 (5)
C(2)–C(3)	1·515 (3)	1·526 (4)	1·527 (5)
C(3)–C(4)	1·548 (2)	1·547 (3)	1·547 (4)
C(3)–O(11)	1·434 (3)	1·430 (3)	1·420 (4)
C(4)–C(5)	1·539 (3)	1·541 (4)	1·548 (4)
C(4)–O(12)	1·439 (2)	1·443 (3)	1·431 (3)
C(4)–C(13)	1·526 (3)	1·523 (4)	1·524 (5)
C(5)–C(6)	1·508 (3)	1·500 (3)	1·505 (4)
C(5)–C(10)	1·536 (2)	1·542 (4)	1·537 (4)
C(6)–C(7)	1·328 (3)	1·336 (4)	1·336 (4)
C(7)–C(8)	1·492 (3)	1·483 (4)	1·492 (4)
C(7)–C(14)	1·525 (2)	1·532 (3)	1·518 (4)
C(8)–C(9)	1·503 (3)	1·508 (4)	1·519 (4)
C(8)–O(18)	1·222 (3)	1·232 (3)	1·215 (4)
C(9)–C(10)	1·531 (3)	1·533 (4)	1·535 (4)
C(10)–C(19)	1·531 (3)	1·538 (4)	1·530 (4)
C(14)–O(15)	1·429 (2)	1·442 (4)	1·443 (4)
C(14)–C(16)	1·524 (3)	1·503 (5)	1·520 (5)
C(14)–C(17)	1·526 (3)	1·526 (5)	1·528 (5)
C(1)–H(1*a*)	0·96 (3)	0·94 (3)	1·01 (5)
C(1)–H(1*b*)	0·99 (3)	0·91 (4)	0·98 (5)
C(2)–H(2*a*)	0·99 (3)	0·93 (3)	0·90 (6)
C(2)–H(2*b*)	0·99 (4)	1·02 (4)	0·95 (5)
C(3)–H(3)	1·05 (3)	1·00 (4)	1·01 (3)
C(5)–H(5)	1·05 (2)	0·98 (3)	1·04 (4)
C(6)–H(6)	1·06 (2)	1·01 (5)	0·96 (4)
C(9)–H(9*a*)	0·81 (3)	0·99 (5)	1·01 (5)
C(9)–H(9*b*)	1·09 (3)	0·99 (3)	1·01 (4)
O(11)–H(11)	0·95 (3)	0·76 (6)	0·94 (6)
O(12)–H(12)	0·98 (3)	0·78 (5)	0·76 (5)
C(13)–H(13*a*)	1·12 (3)	1·01 (4)	0·99 (6)
C(13)–H(13*b*)	0·88 (4)	1·04 (5)	1·07 (4)
C(13)–H(13*c*)	1·02 (5)	1·06 (6)	0·95 (4)
O(15)–H(15)	0·70 (6)	0·85 (7)	0·67 (5)
C(16)–H(16*a*)	1·02 (5)	1·01 (5)	1·00 (6)
C(16)–H(16*b*)	0·99 (5)	1·04 (4)	1·02 (7)
C(16)–H(16*c*)	0·97 (3)	1·00 (4)	1·02 (5)
C(17)–H(17*a*)	1·26 (9)	0·91 (6)	1·05 (5)
C(17)–H(17*b*)	1·07 (5)	1·05 (5)	0·89 (5)
C(17)–H(17*c*)	1·18 (10)	0·93 (5)	0·94 (6)
C(19)–H(19*a*)	1·06 (4)	0·98 (5)	1·00 (6)
C(19)–H(19*b*)	0·77 (4)	0·90 (4)	1·04 (7)
C(19)–H(19*c*)	0·95 (3)	0·95 (5)	1·00 (6)
O(20)–H(20*a*)	0·91 (4)	0·98 (5)	
O(20)–H(20*b*)	0·92 (6)	0·99 (5)	

Table 4. *Valence angles* (°)

	Plucheinol	(3αH)-Plucheinol Molecule 1	Molecule 2
C(2)C(1)C(10)	111·9 (2)	111·9 (2)	112·3 (3)
C(1)C(2)C(3)	111·3 (2)	112·1 (2)	112·6 (3)
C(2)C(3)C(4)	112·9 (1)	112·6 (2)	113·0 (2)
C(2)C(3)O(11)	110·6 (2)	107·8 (2)	107·8 (3)
C(4)C(3)O(11)	109·9 (1)	108·8 (2)	110·7 (2)
C(3)C(4)C(5)	107·2 (1)	108·0 (2)	109·2 (2)
C(3)C(4)O(12)	108·1 (1)	109·1 (2)	109·2 (2)
C(3)C(4)C(13)	113·2 (2)	111·2 (2)	110·0 (2)
C(5)C(4)O(12)	105·3 (1)	108·7 (2)	107·4 (2)
C(5)C(4)C(13)	114·8 (1)	115·7 (2)	115·5 (2)
O(12)C(4)C(13)	107·7 (1)	103·9 (2)	105·4 (2)
C(4)C(5)C(6)	113·6 (1)	113·7 (2)	112·9 (2)
C(4)C(5)C(10)	116·2 (1)	116·0 (2)	116·5 (2)
C(6)C(5)C(10)	111·0 (1)	112·2 (2)	112·3 (2)
C(5)C(6)C(7)	124·9 (2)	124·2 (2)	124·2 (2)
C(6)C(7)C(8)	118·2 (2)	118·5 (2)	118·3 (2)
C(6)C(7)C(14)	122·6 (2)	122·9 (2)	122·9 (2)
C(8)C(7)C(14)	119·2 (2)	118·6 (2)	118·7 (2)
C(7)C(8)C(9)	117·5 (2)	117·9 (2)	117·2 (2)
C(7)C(8)O(18)	122·0 (2)	121·7 (2)	122·9 (3)
C(9)C(8)O(18)	120·5 (2)	120·3 (2)	119·9 (3)
C(8)C(9)C(10)	113·1 (2)	112·1 (2)	113·6 (3)
C(1)C(10)C(5)	108·4 (1)	108·3 (2)	107·5 (2)
C(1)C(10)C(9)	110·7 (2)	109·8 (2)	110·3 (3)
C(1)C(10)C(19)	109·5 (2)	110·3 (2)	110·5 (2)
C(5)C(10)C(9)	105·3 (2)	105·3 (2)	104·3 (2)
C(5)C(10)C(19)	115·3 (2)	115·1 (2)	115·9 (3)
C(9)C(10)C(19)	107·6 (2)	107·8 (2)	108·2 (2)
C(7)C(14)O(15)	109·9 (2)	110·4 (2)	105·9 (2)
C(7)C(14)C(16)	111·7 (2)	112·0 (2)	112·6 (2)
C(7)C(14)C(17)	110·6 (2)	109·6 (2)	110·5 (2)
O(15)C(14)C(16)	104·8 (2)	104·2 (3)	108·2 (3)
O(15)C(14)C(17)	108·9 (2)	110·0 (2)	108·3 (2)
C(16)C(14)C(17)	110·8 (2)	110·6 (3)	111·1 (2)

Table 5. *Torsion angles* (°)

	Plucheinol	(3αH)-Plucheinol Molecule 1	Molecule 2
1–2–3–4	−57·9 (2)	−55·7 (3)	−53·4 (4)
2–3–4–5	53·6 (2)	52·5 (3)	48·7 (3)
3–4–5–10	−53·7 (2)	−54·2 (2)	−51·9 (3)
4–5–10–1	54·6 (2)	55·4 (3)	54·9 (3)
5–10–1–2	−54·3 (2)	−54·2 (3)	−55·5 (3)
10–1–2–3	57·7 (2)	56·5 (3)	57·1 (4)
5–6–7–8	0·6 (3)	−1·0 (4)	−0·1 (4)
6–7–8–9	2·1 (3)	5·7 (3)	1·9 (4)
7–8–9–10	−33·9 (3)	−36·8 (3)	−33·6 (4)
8–9–10–5	59·3 (2)	59·3 (2)	58·7 (3)
9–10–5–6	−55·1 (2)	−54·2 (2)	−55·7 (3)
10–5–6–7	28·1 (3)	27·4 (3)	29·5 (4)
1–2–3–O(11)	178·6 (2)	64·3 (3)	69·3 (3)
2–3–4–O(12)	166·7 (2)	170·5 (3)	165·9 (3)
2–3–4–13	−74·0 (2)	−75·5 (3)	−79·0 (4)
O(11)–3–4–O(12)	−69·3 (2)	51·0 (2)	44·8 (3)
O(11)–3–4–13	50·0 (2)	165·1 (2)	159·9 (3)
O(11)–3–4–5	177·5 (2)	−67·0 (3)	−72·4 (3)
5–6–7–14	−178·6 (3)	−179·3 (3)	177·3 (4)
6–7–14–15	−1·6 (3)	−136·1 (3)	5·3 (4)
6–7–14–16	−117·4 (3)	−20·5 (3)	123·5 (4)
6–7–14–17	118·7 (3)	102·7 (3)	−111·7 (4)
14–7–8–O(18)	0·3 (3)	2·2 (2)	1·9 (4)
6–7–8–O(18)	−178·9 (2)	−176·2 (3)	179·5 (4)
9–8–7–14	−178·7 (3)	−175·9 (3)	−175·7 (4)
8–7–14–O(15)	179·3 (2)	45·7 (3)	−177·2 (4)
8–7–14–16	63·4 (3)	161·2 (3)	−59·0 (4)
8–7–14–17	−60·5 (3)	−75·6 (3)	65·8 (8)

alternate least-squares and difference-Fourier calculations. The structure was refined by full-matrix least-squares techniques to a final R of 0·050.

A final difference-Fourier map showed no peak larger than 0·2 e Å^{-3} for plucheinol and 0·3 e Å^{-3} for (3αH)-plucheinol. No shift during the final refinement was greater than 0·6σ for plucheinol or 0·3σ for (3αH)-plucheinol. Atomic scattering factors for the real and imaginary parts of the anomalous dispersion were calculated by the XRAY76 program (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic positional parameters for plucheinol and (3αH)-plucheinol are given in Tables 1 and 2, while interatomic distances, valence angles and torsion angles are presented in Tables 3, 4 and 5.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36291 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

Figs. 1 and 2 are *ORTEP* drawings (Johnson, 1965) of plucheinol and (3αH)-plucheinol (molecule 1). The cyclohexane rings in both compounds exhibit chair conformations with the C(4) hydroxyl groups occupying equatorial sites. The C(3) hydroxyl group in plucheinol is equatorial while it is axial in the epimer. The cyclohexane rings are *trans*-fused to cyclohexenone rings which exhibit 1,2-diplanar (puckered sofa) conformations. The methyl groups at C(4) and C(10) occupy axial sites on the same face of the cyclohexane

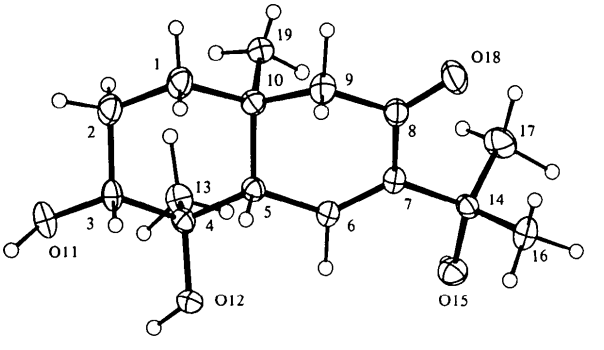

Fig. 1. *ORTEP* (Johnson, 1965) drawing of plucheinol. Thermal ellipsoids are drawn at 35% probability level. Isotropic hydrogen atom thermal parameters are shown as spheres of arbitrary size.

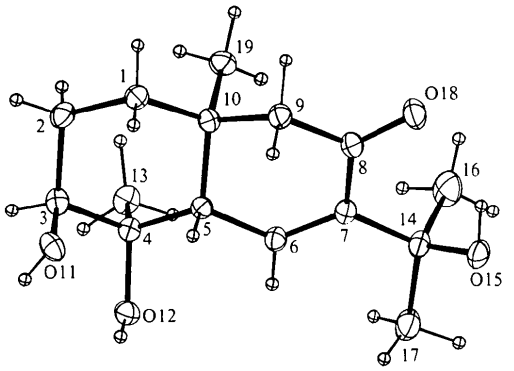

Fig. 2. *ORTEP* drawing of (3αH)-plucheinol (molecule 1). Thermal ellipsoids are drawn at 35% probability level. Isotropic hydrogen atom thermal parameters are shown as spheres of arbitrary size.

Table 6. *Possible hydrogen bonds (values in* Å)

Plucheinol			
$H_2O(20)\cdots O(12)$	2·801 (3)	$H(20a)\cdots O(12)$	1·88 (4)
$H_2O(20)\cdots O(11)$ $(x, y, z-1)$	2·738 (3)	$H(20b)\cdots O(11)$	1·83 (6)
$H_2O(20)\cdots O(11)$ $(1·5-x, 1-y, z-0·5)$	2·754 (3)	$O(20)\cdots H(11)$	1·80 (4)
$H_2O(20)\cdots O(15)$ $(0·5-x, 1-y, z+0·5)$	2·869 (3)	$O(20)\cdots H(15)$	2·17 (6)
$O(12)\cdots O(15)$ $(0·5-x, 1-y, z+0·5)$	2·770 (2)	$H(12)\cdots O(15)$	1·78 (3)
(3αH)-Plucheinol			
$H_2O(20)\cdots O(11)$	2·676 (3)	$O(20)\cdots H(11)$	1·94 (5)
$H_2O(20)\cdots O(12)'$	2·748 (3)	$H(20b)\cdots O(12)'$	2·14 (8)
$H_2O(20)\cdots O(11)'$ $(1-x, y-0·5, 1-z)$	2·812 (3)	$H(20a)\cdots O(11)'$	1·86 (6)
$H_2O(20)\cdots O(15)$ $(-x, 0·5+y, 1-z)$	2·999 (3)	$O(20)\cdots H(15)$	2·44 (7)
$O(15)'\cdots O(12)$ $(x+1, y, z)$	2·940 (3)	$H(15)'\cdots O(12)$	2·28 (5)
$O(12)\cdots O(11)$	2·741 (3)	$H(12)\cdots O(12)$	2·43 (6)
$O(18)\cdots O(15)$	2·757 (3)	$O(18)\cdots H(15)$	2·04 (6)
$O(12)'\cdots O(11)$ $(1-x, 0·5+y, 1-z)$	2·835 (7)	$H(12)'\cdots O(11)$	2·11 (5)
$O(11)'\cdots O(15)$ $(-x, 0·5+y, 1-z)$	2·777 (3)	$H(11)'\cdots O(15)$	1·85 (6)

' Indicates molecule 2 of (3αH)-plucheinol.

ring. Atoms C(5) to C(9) with C(14) and O(18) form a planar system. For plucheinol and molecule 2 of (3αH)-plucheinol the hydroxyl O(15) is coplanar and in a *cis* orientation with C(6)C(7)C(14) with torsion angles of −1·6 (3) and 5·3 (4)°. There is extensive hydrogen bonding in the two structures and O(15) in molecule 1 is twisted out of the plane to maximize hydrogen-bond formation. A listing of possible hydrogen bonds is given in Table 6. In plucheinol and molecule 2 of the epimer the C(16) and C(17) methyl groups are bisected by O(18).

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Salignone-A and Salignone-H, Two Diterpene Dilactones

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Abstract

Salignone-H and salignone-A are nor- and bisnor-diterpene dilactones isolated from *Podocarpus saligna*. The compounds crystallize in the monoclinic space group $P2_1$ with $a = 10·469$ (4), $b = 11·337$ (2), $c = 6·764$ (2) Å, $\beta = 104·70$ (2)°, $V = 776·5$ (4) Å^3, $Z = 2$, $d_c = 1·481$ Mg m^{-3}, and $\mu = 0·980$ mm^{-1} for salignone-A and $a = 11·921$ (6), $b = 7·686$ (3), $c = 9·848$ (5) Å, $\beta = 112·02$ (4)°, $V = 836·5$ (6) Å^3, $Z =$

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