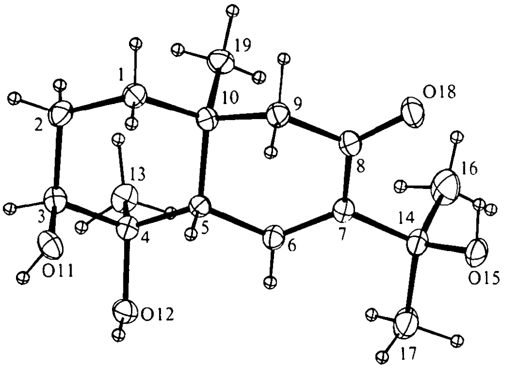

Fig. 2. *ORTEP* drawing of (3αH)-plucheinol (molecule 1). Thermal ellipsoids are drawn at 35% probability level. Isotropic hydrogen atom thermal parameters are shown as spheres of arbitrary size.

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

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

Chiang, M. T., Bittner, M., Silva, M. & Watson, W. H. (1979). *Rev. Latinoam. Quím.* **10**, 95–96.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Hamilton, W. (1965). *Acta Cryst.* **18**, 502–510.

Ivie, R. A., Watson, W. H. & Dominguez, X. A. (1974). *Acta Cryst.* B**30**, 2891–2897.

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

Langs, D. A. & De Titta, G. T. (1975). *Acta Cryst.* A**31**, S16.

Nakanishi, K., Crouch, R., Miura, I., Dominguez, X. A., Zamudio, A. & Villarreal, R. (1974). *J. Am. Chem. Soc.* **96**, 609–611.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). XRAY76. Tech. Rep. TR441, Computer Science Center, Univ. of Maryland, College Park, Maryland.

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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 $a = 10{\cdot}469$ (4), $b = 11{\cdot}337$ (2), $c = 6{\cdot}764$ (2) Å, $\beta = 104{\cdot}70$ (2)°, $V = 776{\cdot}5$ (4) Å^3, $Z = 2$, $d_c = 1{\cdot}481$ Mg m^{-3}, and $\mu = 0{\cdot}980$ mm^{-1} for salignone-A and $a = 11{\cdot}921$ (6), $b = 7{\cdot}686$ (3), $c = 9{\cdot}848$ (5) Å, $\beta = 112{\cdot}02$ (4)°, $V = 836{\cdot}5$ (6) Å^3, $Z =$

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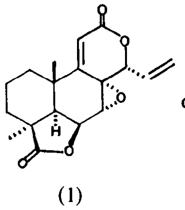
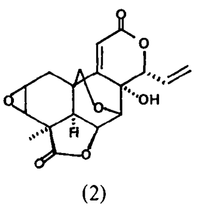
2, d_c = 1·375 Mg m^{-3} and μ = 0·859 mm^{-1} for salignone-H. The structure of salignone-A was solved through the use of the direct-methods program *MULTAN* while that of salignone-H could only be solved through the use of *QTAN*. Both structures were refined by full-matrix least-squares techniques (non-hydrogen atoms anisotropic, H atoms isotropic) to final R values of 0·034 (1080 reflexions) and 0·056 (1514 reflexions), respectively. The A and B rings are *trans*-fused with the A rings exhibiting 1,2-diplanar conformations. The two six-membered B rings differ considerably in conformation due to a change in configuration at C(7) and a fusion of axial substituents O(7) and C(19) in salignone-A. The α,β-unsaturated δ-lactones are in distorted 1,3-diplanar conformations while the five-membered γ-lactones exhibit flattened envelope conformations.

Introduction

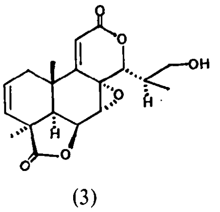
Nor- and bisnorditerpene dilactones, isolated from *Podocarpus* species, exhibit a variety of biological activities (Zabel, Watson, Silva, Bittner & Langs, 1980). *Podocarpus saligna* D. Don is one of three species of *Podocarpus* native to Chile. The leaves do not elicit insect-moulting behavior; however, the plant has not been screened for other types of activity. The identification of the constituents daucosterin, fern-9(11)-ene, isofernene, β-sitosterol and n-nonacosane were reported in an earlier publication (Bhakuni, Bittner, Sammes & Silva, 1974). At least eight nor- and bisnorditerpene dilactones have been isolated subsequently from the roots and leaves of *P. saligna*; however, the compounds are difficult to purify and only small samples are available for characterization. We reported previously the structure of salignone-D (1) (Zabel, Watson, Silva, Bittner & Langs, 1980) and now describe the structures of the two additional terpenes salignone-A (2) and salignone-H (3).



(1)



(2)



(3)

Structure determination and refinement

All intensity data were collected on a Syntex $P2_1$ diffractometer by the θ:2θ scanning technique using a variable scan speed, a graphite monochromator and 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. Systematic absences were consistent with space group $P2_1$ for both structures. 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* (×10^4, *for* H ×10^3) *and isotropic thermal parameters* (Å^2) *for salignone-A*

	x	y	z	U_{eq}/U*
C(1)	4835 (3)	671 (3)	8994 (4)	3·5
C(2)	6205 (3)	894 (3)	10234 (3)	3·9
C(3)	7151 (3)	1604 (2)	9474 (4)	3·5
O(3)	6501 (2)	2104 (2)	10918 (2)	4·1
C(4)	6769 (3)	2081 (2)	7316 (3)	2·9
C(5)	5373 (3)	1747 (2)	6055 (3)	2·5
C(6)	4958 (3)	2819 (2)	4656 (3)	2·7
O(6)	5768 (2)	3800	5683 (3)	3·1
C(7)	3525 (3)	3120 (2)	4484 (3)	2·9
O(7)	3350 (2)	3528 (2)	6380 (3)	3·4
C(8)	2715 (3)	1985 (2)	3897 (3)	2·9
O(8)	3169 (2)	1446 (2)	2299 (2)	3·4
C(9)	3045 (3)	1231 (2)	5813 (3)	2·9
C(10)	4330 (3)	1571 (2)	7283 (3)	2·7
C(11)	2152 (3)	452 (3)	6100 (4)	4·0
C(12)	893 (4)	304 (3)	4561 (4)	4·7
O(12)	188 (3)	−543 (3)	4527 (3)	7·1
O(13)	514 (2)	1120 (2)	3086 (3)	4·5
C(14)	1244 (3)	2234 (3)	3230 (4)	3·6
C(15)	847 (3)	2779 (3)	1146 (4)	4·7
C(16)	432 (5)	3864 (4)	833 (6)	6·6
C(17)	6728 (3)	3421 (2)	7260 (3)	3·0
O(17)	7449 (2)	4101 (2)	8379 (3)	3·9
C(18)	7813 (3)	1703 (3)	6190 (4)	4·0
C(19)	3980 (3)	2781 (2)	8071 (4)	3·4
H(1*a*)	476 (3)	−5 (4)	844 (5)	4·4
H(1*b*)	422 (4)	62 (3)	983 (5)	4·3
H(2)	655 (5)	35 (5)	1127 (6)	6·7
H(3)	804 (4)	150 (3)	1000 (4)	3·0
H(5)	543 (3)	102 (2)	535 (4)	2·4
H(6)	508 (4)	271 (4)	318 (6)	6·6
H(7)	325 (3)	376 (3)	357 (4)	3·3
H(8)	290 (5)	72 (5)	226 (6)	6·5
H(11)	229 (4)	−12 (4)	720 (6)	5·4
H(14)	95 (3)	268 (3)	410 (5)	3·3
H(15)	91 (4)	217 (4)	−11 (6)	6·6
H(16*a*)	31 (6)	426 (7)	−53 (9)	11·8
H(16*b*)	27 (6)	433 (7)	199 (9)	9·8
H(18*a*)	786 (4)	81 (4)	616 (5)	5·1
H(18*b*)	764 (5)	203 (4)	456 (6)	7·1
H(18*c*)	868 (4)	197 (3)	690 (4)	3·4
H(19*a*)	335 (3)	270 (2)	886 (3)	1·6
H(19*b*)	478 (4)	312 (4)	886 (5)	4·5

* For nonhydrogen atoms $U_{eq} = (U_1U_2U_3)^{1/3}$ (e.s.d.'s: 0·1–0·2 Å^2, for H atoms 0·6–2·1 Å^2).

Salignone-A ($C_{18}H_{18}O_7$, M_r = 346·34)

A crystal of dimensions 0·05 × 0·2 × 0·6 mm was used to collect 1101 independent reflexions of which 21 had intensities of less than $2\sigma(I)$ and were excluded from the refinement. The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the $|E|$ values greater than 1·3. The phase set with the highest combined figure of merit was selected and an E map calculated with these phases revealed the positions of most nonhydrogen atoms. After several cycles of least-squares refinement H atoms were located in a difference Fourier map. The structure was refined to a final R of 0·034 by a full-matrix least-squares technique with nonhydrogen atoms refined anisotropically. R is defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(I)$ was estimated from counting statistics. The largest peak in a final difference Fourier map was 0·2 e Å^{-3} and the average shift/error was 0·08. The atomic positional parameters and the U_{eq} values are listed in Table 1 while bond distances, valence angles and torsion angles are given in Tables 3, 4 and 5.

Table 2. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* (Å^2) *for salignone-H*

	x	y	z	U_{eq}/U*
C(1)	3091 (3)	6720 (4)	7522 (4)	5·3
C(2)	1946 (4)	6047 (8)	7634 (8)	9·0
C(3)	1522 (3)	4427 (6)	7243 (5)	6·8
C(4)	2158 (2)	3159 (5)	6602 (3)	4·8
C(5)	3265 (2)	3918 (4)	6376 (3)	4·0
C(6)	3988 (2)	2297 (4)	6370 (3)	4·2
O(6)	3740 (2)	1120 (3)	7374 (2)	5·0
C(7)	5327 (2)	2555 (4)	6798 (3)	4·5
O(7)	5559 (2)	3716 (3)	5784 (2)	4·7
C(8)	5869 (2)	4259 (4)	7295 (3)	4·1
C(9)	5114 (2)	5719 (4)	7454 (3)	3·9
C(10)	3947 (2)	5224 (3)	7610 (3)	4·0
C(11)	5594 (3)	7308 (4)	7598 (3)	4·2
C(12)	6805 (3)	7586 (4)	7577 (3)	4·6
O(12)	7178 (2)	9000 (–)	7405 (3)	5·9
O(13)	7538 (2)	6204 (3)	7745 (2)	4·8
C(14)	7186 (2)	4564 (4)	8217 (3)	4·2
C(15)	8124 (2)	3205 (4)	8296 (3)	4·7
C(16)	9354 (3)	3743 (6)	9439 (4)	6·3
C(17)	2710 (3)	1604 (4)	7558 (3)	5·1
O(17)	2358 (2)	800 (4)	8353 (3)	7·3
C(18)	1218 (3)	2411 (6)	5164 (4)	6·3
C(19)	4382 (2)	4439 (5)	9170 (3)	4·8
C(20)	8219 (3)	2747 (5)	6837 (4)	5·9
O(20)	9008 (3)	1337 (4)	6964 (4)	7·7
H(1*a*)	343 (3)	754 (6)	828 (3)	4·3
H(1*b*)	317 (4)	727 (7)	654 (5)	6·1
H(2)	154 (5)	681 (2)	783 (6)	9·0
H(3)	91 (5)	406 (9)	725 (5)	8·0
H(5)	306 (3)	461 (7)	540 (4)	5·4
H(6)	372 (4)	169 (8)	544 (5)	7·1
H(7)	573 (3)	156 (7)	704 (4)	5·8
H(11)	534 (3)	832 (8)	766 (4)	5·1
H(14)	732 (3)	467 (6)	921 (4)	4·3
H(15)	778 (3)	196 (6)	854 (3)	4·5
H(16*a*)	927 (8)	369 (19)	1046 (12)	18·2
H(16*b*)	968 (5)	459 (12)	912 (6)	8·4
H(16*c*)	1006 (4)	274 (7)	948 (5)	6·7
H(18*a*)	80 (6)	173 (13)	543 (7)	9·6
H(18*b*)	158 (4)	159 (9)	456 (5)	7·6
H(18*c*)	105 (6)	351 (11)	448 (6)	9·1
H(19*a*)	339 (4)	413 (8)	917 (5)	7·2
H(19*b*)	454 (3)	540 (7)	985 (4)	4·9
H(19*c*)	484 (5)	360 (10)	921 (6)	8·0
H(20*a*)	845 (9)	372 (19)	651 (11)	14·3
H(20*b*)	765 (7)	186 (16)	612 (8)	11·0
H(20)	865 (7)	28 (16)	734 (8)	9·6

* For nonhydrogen atoms $U_{eq} = (U_1 U_2 U_3)^{1/3}$ (e.s.d.'s: 0·1–0·3 Å^2, for H atoms 0·8–3·4 Å^2).

Salignone-H ($C_{19}H_{22}O_6$, $M_r = 346{\cdot}38$)

A poor-quality crystal of dimensions 0·1 × 0·65 × 0·4 mm was used to collect 1583 independent reflexions of which 68 were less than $2\sigma(I)$ and were not used in the refinement. One additional reflexion showed significant secondary extinction and was omitted. The structure could not be solved through use of *MULTAN* although numerous starting sets were manually selected. *QTAN* (Langs & DeTitta, 1975) was used to generate and select triples and negative quartets within the set of $|E|$ values greater than 1·4. Cosine-invariant estimating procedures (Hauptman, 1972) were used to remove aberrant triple-phase relationships from the tangent-formula determination. Tangent refinement extended the starting set which defined 30 ambiguities. The lowest NQEST (DeTitta,

Table 3. *Interatomic distances* (Å)

	Salignone-A	Salignone-H
C(1)–C(2)	1·488 (4)	1·502 (7)
C(1)–C(10)	1·532 (3)	1·518 (4)
C(2)–O(3)	1·455 (4)	–
C(2)–C(3)	1·467 (5)	1·345 (7)
C(3)–O(3)	1·440 (4)	–
C(3)–C(4)	1·512 (3)	1·510 (6)
C(4)–C(5)	1·541 (3)	1·533 (4)
C(4)–C(17)	1·520 (3)	1·511 (4)
C(4)–C(18)	1·543 (4)	1·550 (4)
C(5)–C(6)	1·534 (3)	1·516 (4)
C(5)–C(10)	1·543 (4)	1·550 (3)
C(6)–C(7)	1·514 (4)	1·503 (4)
C(6)–O(6)	1·463 (3)	1·450 (4)
O(6)–C(17)	1·337 (3)	1·358 (4)
C(7)–C(8)	1·538 (4)	1·462 (4)
C(7)–O(7)	1·418 (3)	1·442 (4)
O(7)–C(19)	1·441 (3)	–
C(8)–O(8)*	1·424 (3)	1·454 (3)
C(8)–C(9)	1·518 (3)	1·482 (4)
C(8)–C(14)	1·517 (4)	1·509 (3)
C(9)–C(10)	1·506 (3)	1·505 (4)
C(9)–C(11)	1·335 (4)	1·333 (4)
C(10)–C(19)	1·549 (4)	1·548 (4)
C(11)–C(12)	1·467 (4)	1·467 (5)
C(12)–O(12)	1·208 (5)	1·209 (4)
C(12)–O(13)	1·345 (4)	1·345 (4)
O(13)–C(14)	1·466 (4)	1·459 (4)
C(14)–C(15)	1·499 (4)	1·510 (4)
C(15)–C(16)	1·304 (6)	1·533 (4)
C(15)–C(20)	–	1·524 (5)
C(20)–O(20)	–	1·409 (5)
C(17)–O(17)	1·203 (3)	1·191 (5)

* O(7) for salignone-H.

Edmonds, Langs & Hauptman, 1975) indicated the correct set and an *E* map calculated with these phases revealed the positions of all nonhydrogen atoms. A full-matrix least-squares refinement with anisotropic thermal parameters for the nonhydrogen atoms converged to a final *R* of 0·056. The largest peak in the difference Fourier map was 0·3 e Å^{-3} with the average shift/error during the final cycle of 0·20. The atomic positional parameters and U_{eq} values are listed in Table 2 while bond distances, valence angles and torsion angles are listed in Tables 3, 4 and 5. The atomic scattering factors and the real and imaginary parts of the anomalous dispersion were calculated by XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).*

Table 4. *Valence angles* (°)

	Salignone-A	Salignone-H
C(2)C(1)C(10)	114·3 (2)	110·2 (3)
C(1)C(2)C(3)	122·4 (2)	123·5 (5)
C(1)C(2)O(3)	115·9 (2)	–
C(3)C(2)O(3)	59·1 (2)	–
C(2)C(3)O(3)	60·1 (2)	–
C(2)C(3)C(4)	119·9 (2)	121·6 (4)
O(3)C(3)C(4)	117·4 (2)	–
C(2)O(3)C(3)	60·9 (2)	–
C(3)C(4)C(5)	115·3 (2)	114·2 (3)
C(3)C(4)C(17)	112·4 (2)	114·8 (3)
C(3)C(4)C(18)	109·3 (2)	108·4 (2)
C(5)C(4)C(17)	102·4 (2)	101·2 (2)
C(5)C(4)C(18)	110·4 (2)	112·0 (2)
C(17)C(4)C(18)	106·5 (2)	105·8 (3)
C(4)C(5)C(6)	103·1 (2)	102·1 (2)
C(4)C(5)C(10)	115·8 (2)	111·0 (2)
C(6)C(5)C(10)	107·8 (2)	113·8 (2)
C(5)C(6)O(6)	105·7 (2)	104·4 (2)
C(5)C(6)C(7)	110·2 (2)	115·8 (2)
O(6)C(6)C(7)	108·0 (2)	110·9 (2)
C(6)O(6)C(17)	111·2 (1)	110·2 (2)
C(6)C(7)O(7)	110·9 (2)	110·3 (2)
C(6)C(7)C(8)	107·6 (2)	120·1 (3)
O(7)C(7)C(8)	108·5 (2)	60·1 (2)
C(7)O(7)C(19)	112·8 (2)	–
C(7)O(7)C(8)	–	60·6 (2)
C(7)C(8)O(8)*	106·7 (2)	59·3 (2)
C(7)C(8)C(9)	105·1 (2)	120·3 (2)
C(7)C(8)C(14)	111·9 (2)	124·8 (2)
O(8)*C(8)C(9)	111·0 (2)	113·2 (2)
O(8)*C(8)C(14)	111·3 (2)	117·9 (3)
C(9)C(8)C(14)	110·6 (2)	110·8 (2)
C(8)C(9)C(10)	113·0 (2)	116·1 (2)
C(8)C(9)C(11)	118·7 (2)	116·8 (3)
C(10)C(9)C(11)	127·9 (2)	126·6 (3)
C(1)C(10)C(5)	109·7 (2)	107·6 (2)
C(1)C(10)C(9)	114·0 (2)	115·5 (2)
C(1)C(10)C(19)	113·4 (2)	108·6 (3)
C(5)C(10)C(9)	108·3 (2)	108·4 (2)
C(5)C(10)C(19)	109·4 (2)	114·1 (2)
C(9)C(10)C(19)	101·7 (2)	102·8 (2)
C(9)C(11)C(12)	120·6 (2)	121·1 (3)
C(11)C(12)O(12)	122·6 (3)	123·2 (3)
C(11)C(12)O(13)	119·4 (3)	118·7 (3)
O(12)C(12)O(13)	118·0 (3)	118·1 (3)
C(12)O(13)C(14)	119·5 (2)	118·1 (2)
C(8)C(14)O(13)	109·4 (2)	107·5 (2)
C(8)C(14)C(15)	112·0 (3)	120·5 (2)
O(13)C(14)C(15)	106·1 (2)	108·6 (2)
C(14)C(15)C(16)	122·9 (3)	109·7 (3)
C(14)C(15)C(20)	–	115·2 (2)
C(16)C(15)C(20)	–	111·5 (3)
C(4)C(17)O(6)	110·6 (2)	109·7 (3)
C(4)C(17)O(17)	128·0 (2)	129·9 (3)
O(6)C(17)O(17)	121·4 (2)	120·3 (3)
C(15)C(20)O(20)	–	112·2 (3)
O(7)C(19)C(10)	110·4 (2)	–

* O(7) for salignone-H.

Table 5. *Torsion angles* (°)

	Salignone-A	Salignone-H
1–2–3–4	−3·5 (4)	−2·1 (8)
2–3–4–5	−0·9 (4)	−2·9 (5)
3–4–5–10	30·4 (3)	35·4 (3)
4–5–10–1	−54·1 (2)	−62·7 (3)
5–10–1–2	48·5 (3)	56·6 (4)
10–1–2–3	−21·6 (4)	−26·1 (7)
5–6–7–8	−51·4 (2)	4·7 (4)
6–7–8–9	72·4 (2)	3·2 (4)
7–8–9–10	−21·2 (3)	21·0 (3)
8–9–10–5	−45·2 (3)	−49·7 (3)
9–10–5–6	66·1 (2)	57·3 (3)
10–5–6–7	−16·1 (2)	−35·5 (3)
8–9–11–12	1·9 (4)	0·9 (4)
9–11–12–O13	−14·6 (5)	−15·0 (4)
11–12–O13–14	−10·0 (4)	−11·5 (3)
12–O13–14–8	43·1 (4)	46·9 (3)
O13–14–8–9	−52·0 (3)	−58·2 (3)
14–8–9–11	31·7 (3)	36·0 (3)
4–5–6–O6	−22·7 (3)	−32·9 (2)
5–6–O6–17	10·5 (3)	19·9 (2)
6–O6–17–4	6·9 (3)	2·3 (3)
O6–17–4–5	−21·0 (3)	−22·9 (3)
17–4–5–6	25·6 (2)	33·1 (2)
5–6–7–O7	67·1 (2)	−61·7 (3)
6–7–O7–19	−47·9 (3)	–
7–O7–19–10	−15·9 (3)	–
O7–19–10–5	64·9 (3)	–
19–10–5–6	−44·0 (2)	−56·6 (7)
8–9–10–19	70·1 (3)	71·5 (3)
9–10–19–O7	−49·5 (3)	–
19–O7–7–8	70·0 (3)	–
O7–7–8–9	−47·6 (3)	100·6 (3)
6–O6–17–O17	−175·2 (3)	−179·6 (4)
5–4–17–O17	161·2 (3)	159·2 (4)
9–11–12–O12	163·6 (3)	164·5 (3)
14–O13–12–O12	171·7 (3)	169·0 (4)
12–O13–14–15	164·2 (3)	178·8 (4)
9–8–14–15	−169·3 (3)	176·8 (5)
O13–14–15–16	128·7 (4)	62·2 (4)
8–14–15–16	−112·0 (4)	−173·3 (4)
O13–14–15–20	–	−64·6 (5)
8–14–15–20	–	59·9 (6)
14–15–20–O20	–	−173·2 (6)
16–15–20–O20	–	61·0 (6)

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* Lists of structure factors, thermal parameters and distances involving H atoms for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36359 (22 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 salignone-A and salignone-H. The six-membered *A* rings (1—2—3—4—5—10) in both compounds adopt the 1,2-diplanar conformation. The epoxide function is conformationally equivalent to a double bond. The conformations of the two six-membered *B* rings (5—6—7—8—9—10) differ considerably because of the change in configuration at C(7) and the fusion of O(7) to C(19) in salignone-A. The C(7)—C(8) epoxide function in salignone-H imparts a distorted 1,2-diplanar conformation while the *B* ring in salignone-A can be described as a twisted boat. The *C* rings (8—9—11—12—O13—14) are α,β-unsaturated δ-lactones and are best described as distorted 1,3-diplanar conformations. The bond distances around the ring are in excellent agreement. The α,β-unsaturated ketone portion of the *C* ring deviates from planarity as indicated by torsion angles 9—11—12—O12 = 163·6 (164·5), 14—O13—12—O12 = 171·7 (169·0), 8—9—11—12 = 1·9 (0·9), 9—11—12—O13 = −14·6 (−15·0) and 11—12—O13—14 = −10·0° (−11·5°). The five-membered γ-lactones exhibit flattened envelope conformations. The two additional six-membered rings in salignone-A due to the O(7)—C(19) bridge are in twisted boat conformations.

A ^{13}C NMR spectrum of the bulk sample of salignone-H could be interpreted unequivocally as arising from 2,3-dihydrosalignone-H. A mass spectrum of the bulk sample gave an M^+ peak at 438 with a minor peak at 436 while a mass spectrum of the crystal used in the X-ray diffraction study gave an M^+ peak at 436 with no peak at 438. The chromatographically isolated sample is a mixture of the norditerpene dilactones salignone-H and 2,3-dihydrosalignone-H with the latter being the more abundant.

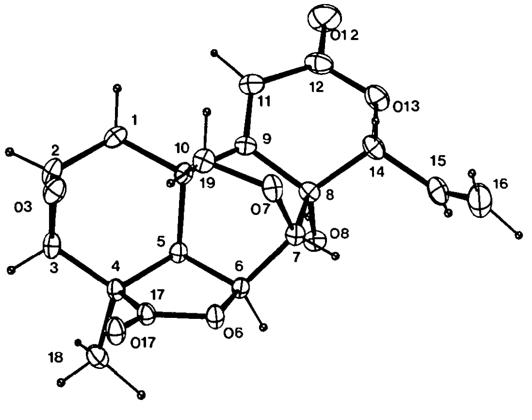

Fig. 1. *ORTEP* drawing of salignone-A. Thermal ellipsoids are drawn at the 35% probability level while H atoms are spheres of arbitrary size.

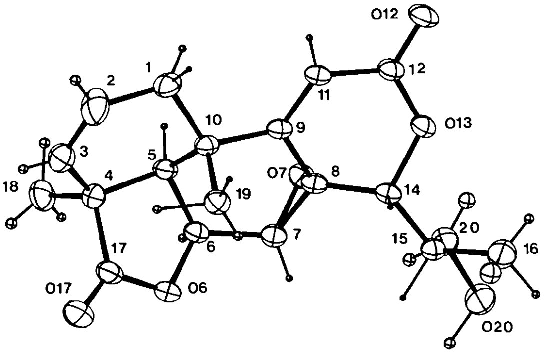

Fig. 2. *ORTEP* drawing of salignone-H. Thermal ellipsoids are drawn at the 35% probability level while H atoms are spheres of arbitrary size.

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References

Bhakuni, D. S., Bittner, M., Sammes, P. G. & Silva, M. (1974). *Rev. Latinoam. Quím.* **5**, 163–168.

DeTitta, G. T., Edmonds, J. W., Langs, E. A. & Hauptman, H. (1975). *Acta Cryst.* A**31**, 472–479.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Hauptman, H. (1972). *Crystal Structure Determination: The Role of the Cosine Seminvariants.* New York: Plenum.

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

Langs, D. A. & DeTitta, G. T. (1975). *Acta Cryst.* A**31**, S16.

Stewart, J. M., Machin, P. A., Dickinson, C., Ammon, H. L., Heck, H. & Flack, H. (1976). XRAY 76. Tech. Rep. TR-441. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Zabel, V., Watson, W. H., Silva, M., Bittner, M. & Langs, D. A. (1980). *Acta Cryst.* B**36**, 2660–2663.