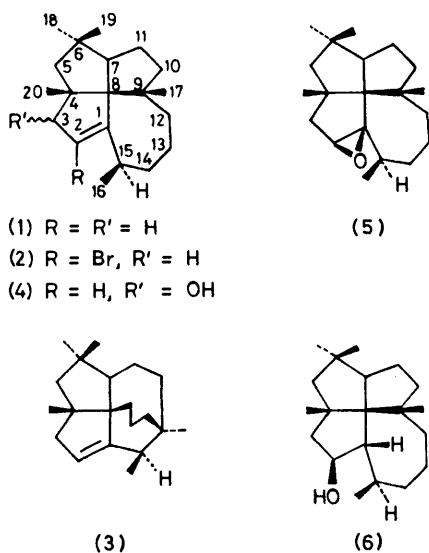


The Structure of Laurenene, a New Diterpene from the Essential Oil of *Dacrydium cupressinum*. Part 2.¹ Crystal Structure

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The structure and absolute configuration of Laurenene (1), a compound possessing a new diterpene skeleton, have been determined by X-ray analysis of the bromo-derivative (2). Crystals are monoclinic, space group P_{2_1} with $a = 7.318(1)$, $b = 13.824(3)$, $c = 9.731(1)$ Å, $\beta = 115.493(5)^\circ$, and $Z = 2$. The structure was solved by the heavy-atom method and the atomic parameters refined by block-diagonal least-squares calculations to R 0.043 over 1 208 independent reflections having $F^2 \geq 2\sigma(F^2)$ from diffractometer measurements. The absolute configuration was established by the anomalous dispersion effect. The cycloheptane ring adopts a twist chair conformation and the double bond suffers from substantial steric crowding.

The diterpene, laurenene, $C_{20}H_{32}$, was fractionated from the essential oil steam-distilled from the leaves and terminal twiglets of *Dacrydium cupressinum*. It was tentatively assigned structure (3) on the basis of chemical



and spectroscopic evidence. Since an unusual diterpene skeleton appeared to be implicated an X-ray analysis of the vinyl bromide, 2-bromolaurenene (2), prepared by bromination of (1) was undertaken. The interrelationship of (1) and (2) was established by the reconversion of (2) to (1) via the Grignard derivative, prepared by the use of active magnesium.²

EXPERIMENTAL

2-Bromolaurenene (2).—A solution of bromine (302 mg) in chloroform (2.5 ml) was added dropwise during 7 min to a stirred solution of the olefin (1) (512 mg) in dry ether (17 ml) at -10° . After stirring at -10° for a further 8 min the solution was warmed to room temperature over 15 min. Removal of solvent and recrystallisation from ethanol gave colourless needles of 2-bromolaurenene (2) (476 mg), m.p. $125-126^\circ$, sublimed at 87° and 0.02 mmHg; ν_{\max} 1 629 (C=CBr) cm^{-1} ; δ 0.99 (3 H, s), 1.02 (3 H, s), 1.07 (3 H, s), 1.34 (3 H, s), 1.40 (3 H, d, J 7 Hz); m/e 350 and 352 (M^+) (Found: C, 68.6; H, 8.9; Br, 23.1. $C_{20}H_{31}Br$ requires C, 68.4; H, 8.9; Br, 22.7%).

Transparent, irregular-shaped crystals of the vinyl bromide (2) were prepared by recrystallisation from hexane.

Reconversion of 2-Bromolaurenene (2) to Laurenene (1).—Anhydrous magnesium chloride (92 mg) and potassium metal (82 mg) were refluxed with stirring in dry tetrahydrofuran (1 ml) under nitrogen for 2 h. The resulting black suspension was cooled to room temperature and a solution of the vinyl bromide (2) (35 mg) in dry tetrahydrofuran (2 ml) added. After stirring under nitrogen at room temperature for 21 h and at reflux temperature for a further 1 h, the mixture was cooled to room temperature, water (5 ml) added, and the products acidified with 2M-sulphuric acid. Ether extraction, drying (Na_2SO_4), and evaporation gave an oil, which, after p.l.c. on silver nitrate-impregnated silica gel with hexane yielded (1) (17 mg) and, at slightly lower R_F , unchanged (2) (8 mg) [identical (i.r., n.m.r., AgNO_3 -t.l.c.) with authentic samples].

Crystal Data.— $C_{20}H_{31}Br$, $M = 351.4$. Monoclinic, $a = 7.318(1)$, $b = 13.824(3)$, $c = 9.731(1)$ Å, $\beta = 115.493(5)^\circ$, $U = 889$ Å³, $D_m(\text{floatation}) = 1.29$ g, cm^{-3} , $Z = 2$, $D_c = 1.31$ g, cm^{-3} , $F(000) = 372$. Mo- K_α radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 24.47$ cm^{-1} . Space group P_{2_1} (C_2) (as confirmed by the subsequent analysis).

Crystallographic Measurements.—Preliminary space-group and unit-cell data were obtained from precession photographs using Cu- K_α radiation and all quantitative X-ray data (Zr-filtered Mo- K_α radiation) from a Hilger and Watts four-circle diffractometer controlled by a PDP 9F computer. A crystal of dimensions ca. $0.40 \times 0.30 \times 0.10$ mm was used for data collection. Unit-cell parameters were obtained by least-squares refinement of the setting angles of 12 reflections accurately centred in a 5-mm diameter circular receiving aperture using an adaptation of the method outlined by Busing.³

The crystal mosaicity was examined by means of open counter ω -scans at a take-off angle of 3° ; the widths at half-height for intense, low-angle reflections ranged from 0.12 to 0.18°. Intensity data were collected in the bisecting mode ($\omega = \theta$). The $\theta-2\theta$ scan technique was used with a symmetric 2θ scan range of 1.44° centred on the calculated peak position and was composed of 72 steps of 1 s. Stationary-crystal-stationary-counter background counts of 18 s were recorded at both ends of the scan. Where necessary, to bring reflections within the linear response range of the scintillation counter, attenuators were automatically inserted in the primary beam. The 5-mm diameter diffracted beam collimator was located with its receiving aperture set 23 cm away from the crystal. Crystal stability was con-

firmed by the constancy of three reference reflections whose intensities were regularly monitored.

A standard deviation was assigned to each measured intensity according to expression (1) where c is the scan

$$\sigma(I) = [c + (t_c/t_b)^2 \cdot (B_1 + B_2) + (pI)^2]^{1/2} \quad (1)$$

count, B_1 and B_2 are the background counts, t_c and t_b are scan and background times respectively, and p is an empirical coefficient⁴ of the nett count I which was given the value 0.05 for the initial refinement. Of the total of 1396 reflections recorded in the quadrant $hk \pm l$ of reciprocal space and $0 < 2\theta < 48^\circ$, 1208 reflections had intensities $I > 2\sigma(I)$. These were corrected for Lorentz and polarisation effects and used in the structure analysis.

TABLE 1
Atom positions

Atom	x/a	y/b	z/c
Br	0.193 0(1)	-0.2500	0.119 9(1)
C(1)	0.527 8(9)	-0.383 3(5)	0.267 9(7)
C(2)	0.349(1)	-0.349 7(5)	0.252 4(8)
C(3)	0.269(1)	-0.395 5(7)	0.354 3(9)
C(4)	0.453(1)	-0.454 9(6)	0.463 4(8)
C(5)	0.601(1)	-0.390 3(6)	0.590 6(8)
C(6)	0.817(1)	-0.422 7(7)	0.629 6(8)
C(7)	0.801(1)	-0.484 2(6)	0.492 1(8)
C(8)	0.581 1(8)	-0.474 0(5)	0.367 0(7)
C(9)	0.540(1)	-0.567 9(5)	0.269 0(9)
C(10)	0.657(1)	-0.644 3(6)	0.389(1)
C(11)	0.840(1)	-0.594 9(6)	0.513(1)
C(12)	0.643(1)	-0.560 7(6)	0.157(1)
C(13)	0.545(1)	-0.498 0(9)	0.017(1)
C(14)	0.587(1)	-0.388 5(8)	0.031(1)
C(15)	0.660(1)	-0.349 5(6)	0.194 2(8)
C(16)	0.691(1)	-0.239 2(8)	0.201 5(9)
C(17)	0.321(1)	-0.596 0(6)	0.176(1)
C(18)	0.955(1)	-0.333 0(7)	0.645(1)
C(19)	0.913(1)	-0.475 0(9)	0.783 2(9)
C(20)	0.391(1)	-0.540 2(7)	0.536(1)

Structure Analysis.—The structure was solved by the heavy atom approach. Initial co-ordinates for the bromine atom were obtained from the three-dimensional Patterson map and positions for the carbon atoms were revealed clearly in a bromine phased (R 0.31) three-dimensional F_0 Fourier synthesis. Several cycles of block-diagonal least squares refinement, with the atoms described by individual, but isotropic, thermal parameters, reduced R to 0.12.

The data were reprocessed with p 0.12 and absorption corrections were applied. Refinement was continued by allowing for anisotropic temperature factors and several cycles reduced R to 0.065. At this stage of the refinement the model was checked to see if the correct enantiomer had been selected. For co-ordinates corresponding to the other enantiomer refinement converged at R 0.060. This highly significant difference⁵ indicates that this reversed model correctly represents the absolute stereochemistry.

Following confirmation that there was significant positive electron-density in a difference-Fourier map at sites calculated for hydrogen atoms (assuming C-H 1.05 Å) these atoms were included with fixed positions and B 4.0 Å in subsequent least-squares iterations. Refinement converged at R 0.043.

A weighting scheme of the form $w = 4F_0^2/\sigma^2(F_0^2)$ was employed. The scattering factor curves used for all atoms were taken from a paper by Cromer and Mann,⁶ the values for bromine being corrected for anomalous dispersion with values $\Delta f'$ and $\Delta f''$.⁷

The minimised function showed little systematic dependence on either F_0 or $\sin\theta$, and a calculation of the structure factors for the reflections having $F_0^2 < 2\sigma(F_0^2)$ revealed no anomalies. Final atom co-ordinates and thermal parameters are in Tables 1–3, bond lengths and bond angles in Tables 4 and 5. The numbering scheme is that of Figure 1. Observed and calculated structure-factor data are deposited in Supplementary Publication No. SUP 22457 (2 pp.).*

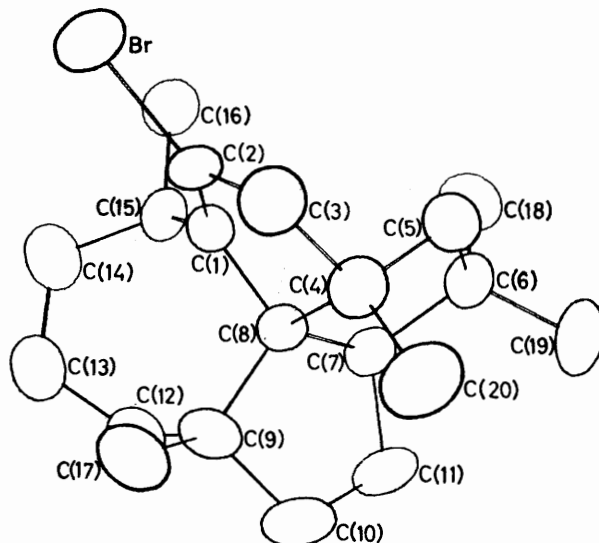


FIGURE 1 Structure and numbering of 2-bromolaurenene (2)

All calculations were carried out at the University of Otago using a Burroughs 6712 computer. The data processing program HILGOUT is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens). Numerical

TABLE 2
Thermal parameters * $\times 10^4$

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Br	280(2)	63(1)	165(1)	53(1)	55(1)	19(1)
C(1)	160(20)	36(4)	87(9)	-4(6)	40(10)	-5(5)
C(2)	190(20)	31(4)	100(10)	21(6)	60(10)	6(5)
C(3)	230(20)	63(5)	140(10)	13(8)	80(10)	4(7)
C(4)	180(20)	53(4)	120(10)	2(7)	70(10)	6(6)
C(5)	230(20)	55(5)	120(10)	16(8)	90(10)	-1(6)
C(6)	210(20)	50(4)	90(10)	-5(7)	50(10)	7(5)
C(7)	190(20)	44(4)	110(10)	10(7)	60(10)	11(5)
C(8)	120(10)	36(3)	96(9)	5(6)	67(9)	3(5)
C(9)	190(20)	39(4)	150(10)	-19(7)	60(10)	-16(6)
C(10)	300(20)	36(4)	210(20)	-1(8)	120(20)	11(7)
C(11)	300(20)	43(4)	180(10)	47(9)	80(20)	30(7)
C(12)	270(20)	60(5)	140(10)	8(9)	80(10)	-19(7)
C(13)	380(30)	81(6)	110(10)	20(10)	110(20)	-12(7)
C(14)	360(30)	85(7)	130(10)	-1(1)	120(20)	-13(8)
C(15)	240(20)	52(5)	90(10)	2(7)	70(10)	13(6)
C(16)	320(20)	60(6)	150(10)	-1(1)	110(10)	13(9)
C(17)	270(20)	58(5)	170(10)	-38(9)	60(20)	-28(7)
C(18)	310(20)	55(5)	170(20)	-48(9)	90(20)	-21(7)
C(19)	340(30)	104(8)	90(10)	20(10)	50(10)	20(8)
C(20)	350(30)	69(6)	210(20)	1(1)	170(20)	30(8)

* The scattering factor is expressed as: $f = f_0 \exp(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

absorption corrections were applied using program ABSORB which is a major modification of the program AGNOST (L. Templeton and D. Templeton). Structure-factor calculations and least-squares refinements were carried out

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1978, Index issue.

TABLE 3

Calculated positions for hydrogen atoms, labelled according to the carbon atom to which they are bonded

Atom	x/a	y/b	z/c
H(3 α)	0.144	-0.442	0.298
H(3 β)	0.226	-0.344	0.418
H(5 α)	0.570	-0.393	0.686
H(5 β)	0.582	-0.317	0.552
H(7)	0.897	-0.453	0.447
H(10 α)	0.697	-0.704	0.342
H(10 β)	0.565	-0.672	0.444
H(11 α)	0.868	-0.618	0.622
H(11 β)	0.971	-0.614	0.494
H(12 α)	0.659	-0.630	0.122
H(12 β)	0.789	-0.530	0.220
H(13 α)	0.384	-0.508	-0.020
H(13 β)	0.582	-0.526	-0.066
H(14 α)	0.454	-0.346	-0.037
H(14 β)	0.698	-0.369	-0.008
H(15)	0.809	-0.378	0.255
H(16 α)	0.574	-0.205	0.107
H(16 β)	0.686	-0.211	0.302
H(16 γ)	0.831	-0.219	0.203
H(17 α)	0.305	-0.634	0.082
H(17 β)	0.268	-0.636	0.244
H(17 γ)	0.234	-0.530	0.143
H(18 α)	0.950	-0.284	0.728
H(18 β)	1.103	-0.352	0.673
H(18 γ)	0.895	-0.294	0.539
H(19 α)	0.967	-0.426	0.872
H(19 β)	0.803	-0.521	0.794
H(19 γ)	1.034	-0.520	0.788
H(20 α)	0.527	-0.576	0.610
H(20 β)	0.320	-0.513	0.601
H(20 γ)	0.299	-0.586	0.453

TABLE 4

Bond lengths (Å)

Br-C(2)	1.896(6)	C(6)-C(19)	1.53(1)
C(1)-C(2)	1.335(9)	C(7)-C(8)	1.548(9)
C(1)-C(8)	1.527(9)	C(7)-C(11)	1.55(1)
C(1)-C(15)	1.505(9)	C(8)-C(9)	1.56(1)
C(2)-C(3)	1.49(1)	C(9)-C(10)	1.53(1)
C(3)-C(4)	1.54(1)	C(9)-C(12)	1.58(1)
C(4)-C(5)	1.53(1)	C(9)-C(17)	1.51(1)
C(4)-C(8)	1.609(9)	C(10)-C(11)	1.52(1)
C(4)-C(20)	1.54(1)	C(12)-C(13)	1.51(1)
C(5)-C(6)	1.53(1)	C(13)-C(14)	1.54(2)
C(6)-C(7)	1.54(1)	C(14)-C(15)	1.54(1)
C(6)-C(18)	1.56(1)	C(15)-C(16)	1.54(1)

TABLE 5

Bond angles (°)

C(2)-C(1)-C(8)	109.2(5)	C(8)-C(7)-C(11)	105.2(6)
C(2)-C(1)-C(15)	129.7(6)	C(1)-C(8)-C(4)	100.3(5)
C(8)-C(1)-C(15)	120.9(5)	C(1)-C(8)-C(7)	117.9(5)
Br-C(2)-C(1)	127.1(5)	C(1)-C(8)-C(9)	111.6(5)
Br-C(2)-C(3)	117.9(5)	C(4)-C(8)-C(7)	102.9(5)
C(1)-C(2)-C(3)	115.0(6)	C(4)-C(8)-C(9)	118.9(5)
C(2)-C(3)-C(4)	102.0(5)	C(7)-C(8)-C(9)	105.6(5)
C(3)-C(4)-C(5)	110.5(7)	C(8)-C(9)-C(10)	102.1(6)
C(3)-C(4)-C(8)	103.9(5)	C(8)-C(9)-C(12)	110.2(6)
C(3)-C(4)-C(20)	112.3(6)	C(8)-C(9)-C(17)	117.1(6)
C(5)-C(4)-C(8)	100.3(5)	C(10)-C(9)-C(12)	107.1(6)
C(5)-C(4)-C(20)	108.7(7)	C(10)-C(9)-C(17)	112.2(7)
C(8)-C(4)-C(20)	120.4(7)	C(12)-C(9)-C(17)	107.6(6)
C(4)-C(5)-C(6)	109.1(6)	C(9)-C(10)-C(11)	107.8(6)
C(5)-C(6)-C(7)	105.0(6)	C(7)-C(11)-C(10)	106.8(6)
C(5)-C(6)-C(18)	110.2(7)	C(9)-C(12)-C(13)	118.3(7)
C(5)-C(6)-C(19)	111.6(6)	C(12)-C(13)-C(14)	118.9(9)
C(7)-C(6)-C(18)	109.1(6)	C(13)-C(14)-C(15)	113.8(8)
C(7)-C(6)-C(19)	114.8(7)	C(1)-C(15)-C(14)	112.0(6)
C(18)-C(6)-C(19)	106.1(7)	C(1)-C(15)-C(16)	113.4(5)
C(6)-C(7)-C(8)	107.5(5)	C(14)-C(15)-C(16)	112.0(6)
C(6)-C(7)-C(11)	119.2(6)		

using program CUCLS and Fourier summations using program FOURIER. These are highly modified versions of the well-known programs ORFLS (W. A. Busing, K. O. Martin, and H. A. Levy) and FORDAP (A. Zalkin), respectively. Interatomic distances and angles and thermal vibration analysis were obtained from program ORFFE also by Busing, Martin, and Levy. DANTEP, a modification of ORTEP by C. K. Johnson, was used for interatomic distance and angle calculations and for production of structure diagrams on an incremental plotter.

DISCUSSION

This X-ray analysis shows that the diterpene has the structure (1), containing a new diterpene skeleton, and the molecular conformation of the bromo-derivative (2) is shown in Figure 1. Torsional angles⁸ are listed in Table 6. Comparison of the cycloheptane ring torsion

TABLE 6

Torsion angles (°)

C(1)-C(8)-C(4)-C(5)	-96	C(12)-C(13)-C(14)-C(15)	-22
C(1)-C(8)-C(4)-C(3)	30	C(13)-C(14)-C(15)-C(16)	177
C(1)-C(8)-C(7)-C(6)	100	C(13)-C(14)-C(15)-C(1)	-49
C(1)-C(8)-C(7)-C(11)	-152	C(14)-C(15)-C(1)-C(2)	-80
C(1)-C(8)-C(9)-C(10)	165	C(14)-C(15)-C(1)-C(8)	94
C(1)-C(8)-C(9)-C(17)	-72	C(15)-C(1)-C(2)-Br	4
C(1)-C(8)-C(9)-C(12)	51	C(15)-C(1)-C(2)-C(3)	-175
C(8)-C(9)-C(10)-C(11)	-32	C(15)-C(1)-C(8)-C(4)	160
C(8)-C(9)-C(12)-C(13)	-76	C(15)-C(1)-C(8)-C(7)	49
C(9)-C(12)-C(13)-C(14)	97	C(15)-C(1)-C(8)-C(9)	-74

TABLE 7

Equations of planes of best fit, in the form $AX + BY + CZ + D = 0$.^{*} Displacements (Å) of atoms from the planes are given in square brackets

Plane (1): Br, C(15), C(1), C(2), C(3), C(4), C(8)

$$-0.2041X - 0.6855Y - 0.6989Z - 1.4256 = 0$$

[Br 0.02, C(15) -0.13, C(1) 0, C(2) 0.03, C(3) 0.05, C(4) -0.24, C(8) 0.26]

Plane (2): C(4)-C(8)

$$0.2390X + 0.8660Y - 0.4393Z + 6.6633 = 0$$

[C(4) -0.24, C(5) 0.17, C(6) -0.03, C(7) -0.12, C(8) 0.22]

Plane (3): C(7)-C(11)

$$0.8405X + 0.0990Y - 0.5328Z - 0.1182 = 0$$

[C(7) 0.11, C(8) -0.20, C(9) 0.22, C(10) -0.15, C(11) 0.03]

^{*} In the equations, X , Y , and Z represent fractional coordinates with respect to the crystallographic axes.

angles with those calculated for twist-chair (C_2) and chair (C_3) conformations⁹ indicates that the ring adopts a conformation which lies closer to a twist-chair form with the approximate C_2 axis passing through C(14). Table 7 lists the planes of best fit and deviations therefrom.

Examination of a model of (2) suggests that the methyl groups bonded to C-4 and C-9 would suffer severe steric interaction. However the C(17)-C(20) distance is found to be quite large (3.41 Å). Twisting of the molecule to avoid this potential interaction is reflected in the long C(4)-C(8) bond and the substantial angle strain present in the five-membered ring containing the double bond.

The considerable steric crowding around the double bond accounts for the low reactivity of laurene (1)

towards addition reactions; for example the lack of hydrogenation using heterogeneous catalysts and the absence of reaction with iodine-silver acetate. In addition, (1) showed considerable resistance to attack by osmic acid; after 31 h at 100°, followed by reductive

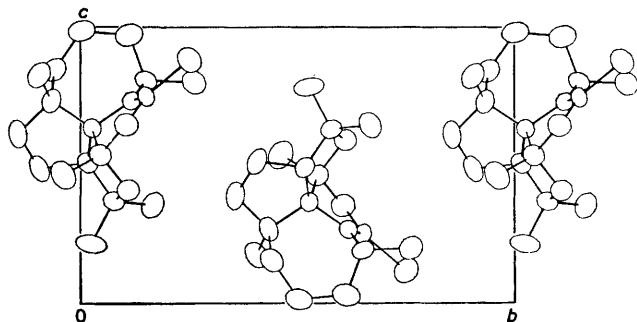


FIGURE 2 Arrangement of molecules in the crystal of 2-bromolaurenene (2) projected along the *a* axis

work-up using lithium aluminium hydride, 77% unchanged (1) was isolated.

No diols could be detected and the remaining components were assigned as the allylic alcohols (4). Models show that attack from the β face* on C(2) would be expected to be less hindered than attack from the α -face. This is consistent with the proposed β -stereo-

* β defined as pointing upwards in (1).

chemistry for the derived epoxide (5) and for the alcohol (6) prepared by hydroboration of (1). Attack at C-1 would be expected to be extremely unfavourable. This is borne out by the course of bromination of (1). Here, neutralisation of the positively charged intermediate by proton removal is more favourable than the conventional attack at C-1 by a bromide ion.

The arrangement of molecules in the crystal as viewed in projection along the *a* axis is shown in Figure 2. Although intramolecular strain in the region of the double bond can be inferred there is no suggestion that intermolecular interactions would be significant in determining the molecular geometry, the shortest intermolecular separation being C(11) \cdots C(16) (3.91 Å).

[8/1041 Received, 5th June, 1978]

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