Absolute Configuration of the (+)-Calamenenes: † Crystal Structure of 7-Hydroxycalamenene ‡

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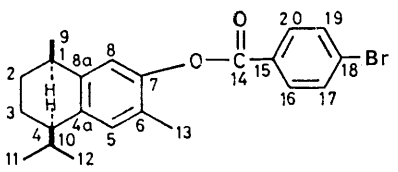
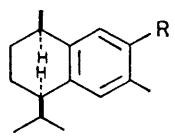
The sesquiterpenes 7-hydroxycalamenene and (+)-calamenene isolated from *Eremophila drummondii* have been interrelated. The crystal structure and absolute configuration of the *p*-bromobenzoate of 7-hydroxycalamenene, $C_{22}H_{25}BrO_2$, has been determined; crystals are orthorhombic, space group $P2_12_12_1$, unit cell dimensions a = 9.471(5), b = 11.469(5), c = 18.253(7) Å, for Z = 4. These results show that both sesquiterpenes have the (1*R*,4*R*)-configurations and resolve the present confusion on this point.

In an investigation of the sesquiterpenes of *Eremophila drummondii* we isolated calamenene and 7-hydroxycalamenene. The structure of these sesquiterpenes was identified by spectroscopic methods and by comparison of their physical properties with those reported in the literature (see later). In attempting to define the relative and absolute stereochemistry of these sesquiterpenes it became evident that contradictory claims had been made regarding the configuration of the common naturally occurring (−)-calamenene. Rowe and Toda [1] established the absolute configuration at C-4 of (−)-calamenene ($[\alpha]_D$ −47°) and 7-hydroxycalamenene as (4*S*)- by interrelation of the latter with the compound derived from (−)-copaene and tentatively suggested that the C-1 methyl was *cis* (1*S*) to the isopropyl group. Andersen *et al.*[2] assigned the *trans*-configuration to the common naturally occurring calamenene and reported the identification of the 1*R*,4*R*-isomer in Alaska cedar oil. These authors also calculated values for the optical rotation of (1*R*,4*R*)-calamenene ($[\alpha]_D$ −22°) and (1*R*,4*S*)-calamenene ($[\alpha]_D$ −96°). However these results were based on studies with inseparable mixtures of *cis*- and *trans*-calamenenes. In view of these contradictory results we decided to obtain unequivocal evidence for the absolute stereochemistry of the calamenenes from *E. drummondii*. This was achieved by carrying out an *X*-ray diffraction study of the *p*-bromobenzoate derivative of 7-hydroxycalamenene which showed it to have



(1)



(2) R = OH
(3) R = $OCOC_6H_3(NO_2)_2$-3,5
(4) R = H

the absolute configuration depicted in (1). 7-Hydroxycalamenene (2) was then converted into calamenene which was identical with a sample of calamenene isolated from *E. drummondii*. In this report we present evidence which shows that the calamenenes isolated from this plant are enantiomeric with the common naturally

† Also known as cadina-1,3,5-trienes (see *Chemical Abstracts* Index Guide); the cadinane numbering system is different from that used here.

‡ The Chemistry of *Eremophila* spp. Part IX. For Part VIII see P. Coates, E. L. Ghisalberti, and P. R. Jefferies, *Austral. J. Chem.*, 1977, **30**, 2717.

[1] J. W. Rowe and J. K. Toda, *Chem. and Ind.*, 1969, 922; and references therein.

[2] N. H. Andersen, D. D. Syrdal, and C. Graham, *Tetrahedron Letters*, 1972, 905.

occurring (−)-calamenene which must now be considered to have the (1*S*,4*S*)-configuration.

Alumina chromatography of the defatted neutral fraction from *E. drummondii* afforded 7-hydroxycalamenene (2) as the major component. The mass spectrum showed a molecular ion peak at *m/e* 218 and a base peak at *m/e* 175. The n.m.r. and u.v. spectra were essentially similar to those reported [1,3] for this compound. The identity of the compound was supported by preparation of the 3,5-dinitrobenzoate derivative (3) which had m.p. 133—135 °C (uncorr.) (lit.[1] 136—137 °C, corr.). A comparison of the optical rotation values of (2) and of its benzoate derivative (3) (27 and 12° respectively) with those reported [1] for 7-hydroxycalamenene isolated from *Ulmus thomasii* and its benzoate derivative (−30° and −10° respectively) indicated an enantiomeric relationship. Careful inspection of the 90 MHz n.m.r. spectra of (2) and (3) showed that these compounds were essentially homogeneous with respect to the stereochemistry of the 1-methyl and 4-isopropyl group.[2,4,5]

For the *X*-ray crystallographic analysis the *p*-bromobenzoate derivative (1) provided suitable crystals. As described later the absolute stereochemistry of 7-hydroxycalamenene was found to be that shown in (1), (1*R*,4*R*), enantiomeric to that of the compound isolated from *U. thomasii*.[1] The 7-hydroxycalamenene from *E. drummondii* was converted into the phenyltetrazoyl ether [3,6] which on hydrogenation at 2 000 p.s.i. was converted to calamenene (4) ($[\alpha]_D$ +43.0°). Separation of the less-polar neutral components of the essential oil from *E. drummondii* by column chromatography afforded a sample of calamenene ($[\alpha]_D$ +41.3°). The similarity in the optical rotation values indicates little or no epimerisation of the labile benzylic centres during hydrogenation. Samples of calamenene isolated following steam distillation of the neutral extract or preparative g.l.c. showed similar rotations (43.7° and 41.9° respectively) to those of the samples already described, again indicating that under these conditions no detectable epimerization had taken place. In general, calamenene occurs in nature as a mixture of diastereoisomers which can however be distinguished by n.m.r.[2,4,5] In all the samples of (1*R*,4*R*)-calamenene (*cis*) obtained by us there was no indication from their high-resolution n.m.r. for the presence of the *trans*-diastereoisomer. Allowing that the limit of detection for the n.m.r. method is *ca.* 10%, then using the known rotation of 82° or 80° reported for the (+)-(1*S*,4*R*)-calamenene (*trans*) [7,8] (assuming that this is the likely diastereomeric contaminant) one can calculate the likely range for the rotation values of the (1*R*,4*R*)-isomers as 37—41.3°.

These results also allow us to clarify the stereochemical outcome of two syntheses of calamenenes. The first [5] involves a sequence starting from dihydrokhusinol, in which the stereochemistry of the 1-methyl substituent does not appear to have been unambiguously assigned. The (+)-calamenene thus obtained showed $[\alpha]_D$ +37.5° and must have the (1*R*,4*R*)-configuration. The second,[7] starting from (−)-menthone, leads to calamenene with $[\alpha]_D$ +43.7° which was later claimed (see ref. 5) to be an 80 : 20 mixture of diastereoisomers. It appears that in fact this synthesis involves equilibration of the isopropyl group largely favouring the (4*R*)-configuration.

EXPERIMENTAL

General experimental details have been described.[9] Analytical g.l.c. was carried out with a Perkin-Elmer 880 gas chromatograph equipped with a copper column (10 ft, ⅛ in o.d.) packed with 5% Carbowax 20M on Chromosorb W (85/100 mesh). Temperature was programmed between 100—210 °C at 8° min^{-1}. Preparative g.l.c. was carried out with a Varian Aerograph Series 1800 gas chromatograph using an aluminium column (10 ft, ⅜ in o.d.) packed with 10% Carbowax 20M on Chromosorb W (60—80 mesh). Temperature was programmed between 135—200° at 4° min^{-1}. Optical rotations were determined with a Perkin-Elmer 141 polarimeter operating at 589 nm for $CHCl_3$ solutions. All identities were confirmed by a comparison of t.l.c., g.l.c., behaviour, n.m.r., and mass spectra.

Isolation of (1R,4R)-7-*Hydroxycalamenene* (2).—Fresh leaves and twigs of *E. drummondii* (1.8 kg) collected near Pithara in Western Australia were washed with ether and the ethereal solution was extracted sequentially with aqueous $NaHCO_3$ (8%) and Na_2CO_3 (5%) solutions. The remaining neutral material (*ca.* 20 g) was recovered by evaporation of the solvent. Part of the neutral extract (10 g) was partitioned between methanol–water (95 : 5) and light petroleum. The material recovered (5 g) from the methanol–water fraction was chromatographed on neutral alumina (Act. II) and elution with light petroleum and light petroleum–5% chloroform gave factions containing *inter alia* (+)-(1*R*,4*R*)-calamenene (see later). Further elution with light petroleum–10% chloroform gave fractions containing (1*R*,4*R*)-7-hydroxycalamenene (2; 2.8 g) as an oil $[\alpha]_D$ 27° (*c* 9.0) (lit.,[1] $[\alpha]_D$ −30° for the 1*S*,4*S*-enantiomer); $\lambda_{max.}$ (nm) 280 (ε 2 500) [lit.[1] 280 (ε 2 480)]; mass spectrometry (*m/e*) 218 (M^+, 10%), 175 (100%), 160 (8%), and 145 (8%); δ (90 MHz, $CDCl_3$) 0.75, 1.00 (d, *J* 7 Hz, isopropyl methyls), 1.16 (d, *J* 7 Hz, C-1 methyl), 1.62 (m, 2- and 3-H_2), 2.18 (s, C-6 methyl), 2.56 (m, 1- and 4-H), 6.15 (brs, O-*H*), 6.53 (s, 8-H), and 6.91 (brs, 5-H) (essentially similar to that reported [1,3]) (Found: C, 82.75; H, 10.05. $C_{15}H_{22}O$ requires: C, 82.50; H, 10.16%).

Derivatives of (1R,4R)-7-*Hydroxycalamenene* (2).—The phenol in pyridine was treated with 3,5-dinitrobenzoyl chloride to give the 3,5-dinitrobenzoate (3) which was recrystallized from n-hexane as needles, m.p. 133—135 °C, $[\alpha]_D$ 12° (*c*, 2.5) {lit.[1] 136—137° (corr), $[\alpha]_D$ −10° (*c*, 1) for the enantiomer}; δ (90 HMz, $CDCl_3$), 0.81, 1.06 (d, *J* 7 Hz,

[3] M. Fracheboud, J. W. Rowe, R. W. Scott, S. M. Fanega, A. J. Buhl, and J. K. Toda, *Forest Product J.*, 1968, **18**, 37.
[4] N. H. Andersen and D. D. Syrdal, *Phytochemistry*, 1970, **9**, 1325.
[5] S. V. Bhatwadekar, K. G. Gore, K. K. Chakravarti, and S. K. Paknikar, *Indian J. Chem.*, 1972, **10**, 1111.
[6] W. J. Musliner and J. W. Gates, *J. Amer. Chem. Soc.*, 1966, **88**, 4271.
[7] P. H. Ladwa, G. D. Joshi, and S. N. Kulkarni, *Chem. and Ind.*, 1968, 1601; and references therein.
[8] G. K. Trivedi, A. D. Wagh, S. K. Paknikar, K. K. Chakravarti, and S. C. Bhattacharyya, *Tetrahedron*, 1966, **22**, 1641.
[9] E. L. Ghisalberti, P. R. Jefferies, T. G. Payne, and G. K. Worth, *Tetrahedron*, 1973, **29**, 403.

isopropyl methyls), 1.27 (d, *J* 7 Hz, C-1 methyl), 2.19 (s, C-6 methyl), 2.97, 2.61 (m, 1- and 4-H), 6.94 (s, 8-H), 7.14 (brs, 5-H), and 9.31 (m, 3 aromatic H) (essentially similar to that reported [1,3]).

The *p-bromobenzoate* (1) was recrystallized from n-hexane as prisms, m.p. 140 °C, $[\alpha]_D$ +23.7° (*c*, 5.2); $\nu_{max.}$ (CCl_4) 1 740 (C=O); mass spectrometry (*m/e*, %) 402, 400 (M^+, 8), 359, 357 (66), 185, and 183 (100); δ (60 MHz, $CDCl_3$) 0.78, 1.02 (d, *J* 7 Hz, isopropyl methyls), 1.25 (d, *J* 7 Hz, C-1 methyl), 2.14 (s, C-6 methyl), 6.84, 7.02 (s, 5- and 8-H), 7.55, and 8.0 (AA'BB' system, aromatic H) (Found: C, 65.60; H, 6.35. $C_{22}H_{25}O_2Br$ requires: C, 65.82; H, 6.28%).

TABLE 1

Atomic fractional cell co-ordinates (× 10^3 for hydrogen, × 10^4 for others)

Atom	*x*	*y*	*z*
C(1)	2 046(21)	7 997(17)	1 977(12)
H(1α)	268(20)	748(14)	181(10)
C(2)	0 668(31)	7 942(19)	1 506(12)
H(2α)	055(25)	722(14)	154(11)
H(2β)	074(18)	856(13)	012(7)
C(3)	−0 534(26)	8 307(19)	1 972(12)
H(3α)	−155(16)	819(14)	162(8)
H(3β)	−049(21)	907(13)	204(9)
C(4)	−0 871(20)	7 623(14)	2 682(9)
H(4α)	−124(14)	665(12)	261(7)
C(4a)	0 514(17)	7 170(13)	3 002(8)
C(5)	0 427(16)	6 517(16)	3 631(8)
H(5)	−059(14)	664(13)	392(7)
C(6)	1 523(16)	5 981(12)	3 990(7)
C(7)	2 837(16)	6 156(12)	3 673(8)
C(8)	2 985(17)	6 802(16)	3 030(9)
H(8)	398(15)	692(12)	278(7)
C(8a)	1 814(17)	7 310(13)	2 676(8)
C(9)	2 568(21)	9 215(15)	2 136(10)
H(9α) *	192(−)	967(−)	247(−)
H(9β) *	354(−)	920(−)	240(−)
H(9γ) *	273(−)	968(−)	168(−)
C(10)	−1 745(19)	8 266(18)	3 216(9)
H(10)	−172(16)	807(13)	376(7)
C(11)	−3 208(17)	8 610(18)	2 910(10)
H(11α) *	−305(−)	918(−)	241(−)
H(11β) *	−377(−)	797(−)	269(−)
H(11γ) *	−384(−)	914(−)	320(−)
C(12)	−1 123(21)	9 400(16)	3 503(9)
H(12α) *	−024(−)	917(−)	378(−)
H(12β) *	−088(−)	994(−)	310(−)
H(12γ) *	−172(−)	986(−)	387(−)
C(13)	1 449(17)	5 269(15)	4 670(9)
H(13α) *	179(−)	441(−)	465(−)
H(13β) *	202(−)	566(−)	506(−)
H(13γ) *	043(−)	523(−)	483(−)
O(7)	4 094(12)	5 606(9)	3 976(6)
C(14)	4 909(22)	6 218(18)	4 399(11)
O(14)	4 867(15)	7 269(12)	4 440(8)
C(15)	6 018(21)	5 489(21)	4 786(9)
C(16)	5 936(24)	4 272(22)	4 796(11)
H(16)	512(16)	387(13)	455(8)
C(17)	6 985(29)	3 720(17)	5 233(15)
H(17)	681(18)	287(12)	518(9)
C(18)	7 993(21)	4 328(24)	5 617(10)
Br	9 220(3)	3 392(2)	6 162(1)
C(19)	7 954(26)	5 495(19)	5 608(13)
H(19)	881(16)	594(13)	583(7)
C(20)	7 027(27)	6 105(19)	5 179(13)
H(20)	719(18)	707(12)	522(8)

* Methyl hydrogen atoms constrained during refinement (see text)

Isolation of (+)-(1R,4R)-*Calamenene* (4).—(*a*) *Column chromatography*. The fractions obtained before elution of 7-hydroxycalamenene (see earlier) were combined and a portion was adsorbed on a column of alumina impregnated with 10% silver nitrate (60 g). Elution with light petroleum yielded fractions of calamenene which were purified by filtration through a column of neutral alumina (Act. I) to give (+)-(1*R*,4*R*)-calamenene as an oil, $[\alpha]_D$ 41.3° (*c*, 1.2), R_t 10 ± 0.5 min; $\lambda_{max.}$ (nm) 224 (ε, 1 300), 270 (ε, 620), and 279 (ε, 680) (similar to those reported [4]); mass spectrometry (*m/e*, %), 202 (M^+, 19), 159 (100), and 145 (19); δ (90 MHz, $CDCl_3$) 0.76, 1.02 (d, *J*, 6.5 Hz, isopropyl methyls), 1.23 (d, *J* 7.1 Hz, C-1 methyl), 2.28 (s, C-6 methyl), 2.53 2.82 (m, 1- and 4-H), and 6.98 (m, 5- and 8-H) (essentially similar to that reported [4,5]) (Found: C, 89 45; H, 11.25. Calc. for $C_{15}H_{22}$: C, 89.03; H, 10.96%).

(*b*) *Steam distillation*. A portion (4.8 g) of the light petroleum soluble fraction of the neutral extract from *E. drummondii* was steam distilled yielding 3.5 ml of oil, which contained 30% calamenene as determined by g.l.c. The oil was adsorbed on neutral alumina (Act. I, 80 g) and eluted with light petroleum and light petroleum–chloroform (gradient up to 5% chloroform). The fractions enriched in calamenene were adsorbed on a column of alumina impregnated with 10% silver nitrate (33 g) and eluted with light petroleum to give fractions of (+)-(1*R*,4*R*)-calamenene (4), $[\alpha]_D$ +43.7° (*c*, 1.0). The n.m.r. spectrum, and g.l.c. and t.l.c. retention time were identical with those of the sample obtained in (*a*).

(*c*) *Preparative g.l.c.* A portion of the fractions from the first column chromatography described in (*a*) was separated

TABLE 2

Molecular geometry (non-hydrogen atoms only)

(*a*) Distances (Å)

C(1)–C(2)	1.56(3)	C(8)–C(8a)	1.41(2)
C(1)–C(8a)	1.52(3)	C(10)–C(11)	1.54(2)
C(1)–C(9)	1.51(3)	C(10)–C(12)	1.52(3)
C(2)–C(3)	1.48(4)	O(7)–C(14)	1.30(2)
C(3)–C(4)	1.55(3)	C(14)–O(14) *	1.21(2)
C(4)–C(4a)	1.53(2)	C(14)–C(15)	1.52(3)
C(4)–C(10)	1.48(3)	C(15)–C(16)	1.40(3)
C(4a)–C(8a)	1.32(2)	C(16)–C(17)	1.42(3)
C(4a)–C(5)	1.37(2)	C(17)–C(18)	1.37(3)
C(5)–C(6)	1.37(2)	C(18)–Br	1.87(2)
C(6)–C(7)	1.39(2)	C(18)–C(19)	1.34(4)
C(6)–C(13)	1.49(2)	C(19)–C(20)	1.37(3)
C(7)–O(7)	1.46(2)	C(15)–C(20)	1.39(3)
C(7)–C(8)	1.40(2)		

(*b*) Angles (°)

C(8a)–C(1)–C(2)	109(2)	C(8)–C(8a)–C(1)	119(1)
C(8a)–C(1)–C(9)	112(2)	C(1)–C(8a)–C(4a)	124(1)
C(2)–C(1)–C(9)	115(2)	C(4)–C(10)–C(11)	113(1)
C(1)–C(2)–C(3)	108(2)	C(4)–C(10)–C(12)	116(2)
C(2)–C(3)–C(4)	120(2)	C(11)–C(10)–C(12)	105(2)
C(2)–C(3)–C(4a)	108(2)	C(7)–O(7)–C(14)	119(1)
C(3)–C(4)–C(10)	114(2)	O(7)–C(14)–O(14)	124(2)
C(4a)–C(4)–C(10)	114(1)	O(7)–C(14)–C(15)	123(2)
C(4)–C(4a)–C(5)	117(1)	O(14)–C(14)–C(15)	113(2)
C(4)–C(4a)–C(8a)	124(1)	C(14)–C(15)–C(16)	121(2)
C(5)–C(4a)–C(8a)	119(1)	C(14)–C(15)–C(20)	116(2)
C(4a)–C(5)–C(6)	127(1)	C(16)–C(15)–C(20)	123(2)
C(5)–C(6)–C(13)	127(1)	C(15)–C(16)–C(17)	114(2)
C(7)–C(6)–C(13)	118(1)	C(16)–C(17)–C(18)	123(2)
C(5)–C(6)–C(7)	114(1)	C(17)–C(18)–C(19)	119(2)
C(6)–C(7)–C(8)	121(1)	C(17)–C(18)–Br	114(2)
C(6)–C(7)–O(7)	121(1)	C(19)–C(18)–Br	127(2)
O(7)–C(7)–C(8)	118(1)	C(18)–C(19)–C(20)	122(2)
C(7)–C(8)–C(8a)	122(1)	C(15)–C(20)–C(19)	119(2)
C(8)–C(8a)–C(4a)	117(1)		

* O(14) has a close contact of 2.3(1) Å to H(19) at $x-1/2, 3/2-y, 1-z$.

by preparative g.l.c. The sample of calamenene thus obtained showed $[\alpha]_D$ 41.9° (*c*, 6.9) and was identical with that obtained in (*a*).

Synthesis of (+)-(1R,4R)-*Calamenene* (4).—7-Hydroxycalamenene (2) (495 mg) in dimethylformamide (18 ml) and K_2CO_3 (2 g) was treated with 1-phenyl-5-chlorotetrazole (1.0 g). The solution was stirred and heated (80 °C) under nitrogen for 1.5 h. The filtered solution was diluted with H_2O and extracted with ether. The product recovered contained unchanged 1-phenyl-5-chlorotetrazole which was found difficult to remove. One quarter of this mixture was taken and the oily tetrazole ether isolated by preparative t.l.c. had the following properties: $[\alpha]_D$ 4.6 (*c*, 1.3); mass spectrometry (*m/e*, %) 362 (M^+, 29), 319 (100), 291 (67), 249 (96), 175 (62), 159 (37), and 117 (100); δ (60 MHz, CCl_4) 0.78, 1.01 (d, *J* 7 Hz, isopropyl methyls), 1.22 (d, *J* 7 Hz, C-1 methyl), 2.15 (s, C-6 methyl), 2.6 (m, 1- and 4-H), 6.95 (s, 5-H), 7.10 (s, 8-H), and 7.6 (brm, phenyl hydrogens). Without further purification the remaining mixture containing the tetrazole ether was dissolved in EtOH and hydrogenated over 10% Pd–C at 200 °C and 2 000 p.s.i. for 2 h. The catalyst was removed by filtration and the solvent evaporated. The residue was taken up in $CHCl_3$ and filtered through neutral alumina (Act. I, 10 g), to give fractions of (+)-(1*R*,4*R*)-calamenene (4; 275 mg) $[\alpha]_D$ 43.0 (*c*, 1.0) identical in all respects with that isolated from *E. drummondii*.

Crystallography.—$C_{22}H_{25}O_2Br$, *M* 401.4. Orthorhombic, $a = 9.471(5)$, $b = 11.469(5)$, $c = 18.253(7)$ Å; *U* 1 983(2) Å^3, $D_m = 1.34(1)$, $Z = 4$, $D_c = 1.34$ g cm^{-3}, $F(000)$ 832, specimen size 0.40 × 0.14 × 0.17 mm. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 20.5 cm^{-1}. Space group $P2_12_12_1$ (D_2^4, No. 19).

Data Collection.—A Syntex $P\bar{1}$ four-circle diffractometer was used, the 2θ—θ mode (2θ < 40°) yielding 1 081 independent reflections of which 667 were considered observed, having $I > 2\sigma(I)$, and used in the structure solution and refinement after absorption correction. Friedel pairs (not reported) were also collected to 2θ < 20° to confirm the absolute configuration. Structure solution was by vector methods. Refinement by block-diagonal least-squares, one block for the parameters of the *p*-bromobenzoate group, one block for each of the other atoms, including associated hydrogen parameters. Thermal parameters were anisotropic for non-hydrogen atoms and isotropic for hydrogen constrained at $\langle U_{ii}(C) + 0.01 \rangle$ Å^3. Hydrogen atoms of non-methyl groups were refined in (*x*, *y*, *z*) only; those of methyl groups were constrained in (*x*, *y*, *z*, *U*). Residuals (on *F*) were *R* 0.056, *R'* 0.053 (other parity: 0.069, 0.069), *S* 1.22. Reflection weights were $w = [\sigma^2(F_o) + 0.000\,6(F_o)^2]^{-1}$. Scattering factors for neutral non-hydrogen atoms, that for bromine corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$), were taken from refs. 10 and 11, those for hydrogen from ref. 12. The '*X*-Ray '76' program system was used,[13] on a CYBER 73 computer. Structure factor amplitudes, thermal parameters, hydrogen geometries are listed in Supplementary Publication No. SUP 22273 (8 pp.).* Carbon atom numbering follows that given for (1), the sequence C(14)—(20) being carried through the carboxy-carbon C(14) and then around the phenyl group. Hydrogen and oxygen atoms follow the labelling of the parent carbon, methyl hydrogens being suffixed α,β,γ.

Final atom co-ordinates are listed in Table 1. The molecular geometry is depicted in the Figure and given in detail in Table 2; deviations from the plane through the calamenene skeleton are shown in Table 3. Because of the bromine content, the skeletal dimensions are relatively imprecise and does not warrant further discussion; in the solid the conformation adopted by the cyclohexane ring is as expected from consideration of the interactions between the ring alkyl substituents and the aromatic *peri*-hydrogen atoms. Likewise, the disposition of the isopropyl group is also consistent with minimum interaction energy requirements.

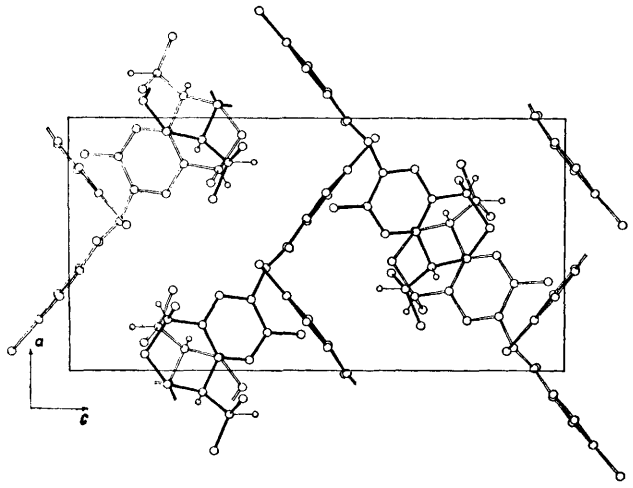


FIGURE Unit-cell contents projected down *b*; hydrogen atoms are only shown where they assist in defining critical stereochemical features. The axes are right-handed

TABLE 3

Deviations (Å) of atoms from the least-squares plane through the calamenene skeleton

Atoms defining plane: C(1), C(4)—(8), C(4a), C(8a), C(13), O(7)
Deviations: C(1) −0.01, C(4) −0.04, C(4a) 0.03, C(5) 0.02, C(6) 0.00, C(7) 0.02. C(8) 0.02, C(8a) 0.00, C(13) −0.01, O(7) −0.04, C(9) 1.37, C(2) −0.70, C(3) −0.05, C(10) 0.99, C(11) 0.82, C(12) 2.43

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* For details see *J.C.S. Perkin 1*, 1977, Index issue.

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