

Crystal Structure and Absolute Configuration of 2 α ,6,6,8-Tetramethyltricyclo[6.2.1.0^{1,5}]undecan-7 β -yl *p*-Bromobenzoate

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The crystal structure of the *p*-bromobenzoate ester of a new tricyclic sesquiterpene alcohol isolated from *Eremophila georgei*, C₂₂H₂₉BrO₂, has been determined from X-ray diffractometer data by the heavy-atom method and refined by least squares to R 0.049 for 1 689 reflections. Crystals of the derivative are monoclinic, space group $P2_1$, $a = 6.341(2)$, $b = 15.560(4)$, $c = 20.475(4)$ Å, $\beta = 95.19(2)^\circ$, $Z = 4$. There are two molecules in the asymmetric unit. The absolute configuration suggested for the tricyclic skeleton is the enantiomer of that reported for khusimol *p*-bromobenzoate.

THIS paper describes the elucidation by X-ray crystallography of the crystal and molecular structure and absolute configuration of a new tricyclic sesquiterpene alcohol isolated from the Australian plant *Eremophila georgei*. This alcohol and the corresponding ketone co-occur in *E. georgei* with other sesquiterpenes of the zizaene series.¹ Preliminary spectroscopic data suggested that this alcohol contained a novel skeleton but the small amount available precluded a chemical solution to the structure. For crystallographic purposes the alcohol was treated with *p*-bromobenzoyl chloride, giving the *p*-bromobenzoate derivative, m.p. 122 °C, $[\alpha]_D^{CHCl_3}$, -11° (c , 0.45); a prismatic crystal fragment 0.18 × 0.20 × 0.18 mm was used for the X-ray study.

EXPERIMENTAL

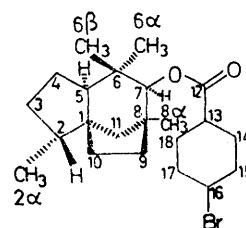
Unit-cell calibration was carried out by a least squares fit of the angular parameters of 15 reflections with 2θ ca. 25° centred in the counter aperture of a Syntex P1 four-circle diffractometer. A unique data set in the range $2\theta < 40^\circ$ was gathered by conventional 2θ - θ scan, yielding 1 978 independent reflections of which 1 689 with $I > \sigma(I)$ were considered 'observed'; a complete set of 'Friedel pairs' was also gathered in the range $2\theta < 30^\circ$. No correction was made for absorption.

Crystal Data.—C₂₂H₂₉BrO₂, $M = 406$. Monoclinic, $a = 6.341(2)$, $b = 15.560(4)$, $c = 20.475(4)$ Å, $\beta = 95.19(2)^\circ$, $U = 2 018(1)$ Å³, $D_m = 1.34(1)$, $Z = 4$. $D_c = 1.34$ g cm⁻³, $F(000) = 848$. Mo- K_α radiation (monochromatic), $\lambda = 0.710 69$ Å; $\mu(\text{Mo-}K_\alpha) = 19.9$ cm⁻¹. Neutral atom scattering factors,^{2,3} that for Br corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).⁴ Space group $P2_1$ (C_2 , No. 3).

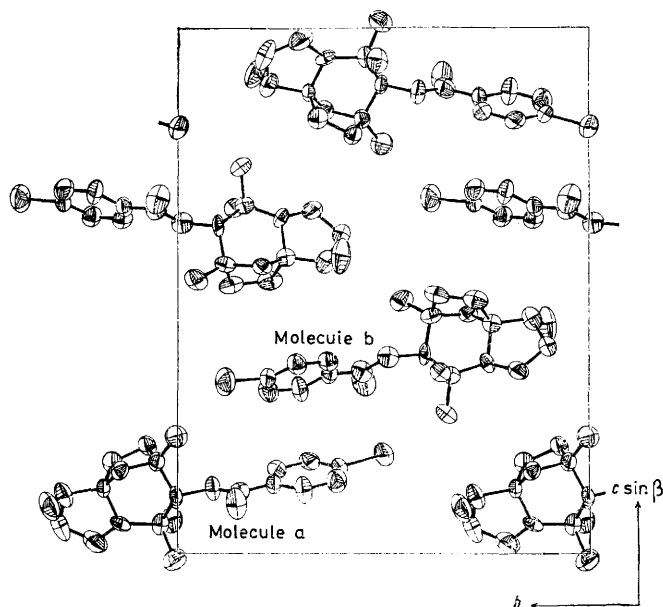
The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least squares with anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} \dots + 2U_{22}k^2b^*c^*)]$. Hydrogen atoms were generally observed in the difference maps but would not refine satisfactorily and their positional parameters were included as invariants with $r(\text{C-H})$ 1.00 Å, U 0.10 Å², those for the methyl groups being in the staggered configuration. At convergence, parameter shifts were $< 0.1 \sigma$, R being 0.049 and $R' [(\sum w ||F_o| - |F_c| |^2) / \sum w |F_o|^2]^{1/2}$ 0.048; the appropriate weighting scheme was of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$ where $n = 6$.

Computation was carried out by use of a local variant of the 'X-Ray '72' system⁵ on a CDC 6200 machine. Struc-

ture amplitudes and Bijvoet pairs are deposited as Supplementary Publication No. SUP 21700 (6 pp., 1 microfiche).*



Results are summarized in Tables 1–4. Atom labelling is as follows: atoms of the two independent molecules in the asymmetric unit are denoted by suffix (a) or (b) where necessary, and hydrogen atoms labelled, where necessary, according to the carbon atom to which they are attached, as are the oxygen atoms.



Unit cell contents projected along a showing 50% thermal ellipsoids. Note that the axial system is right-handed and the absolute configuration as shown.

DISCUSSION

The unit cell (Figure) comprises discrete molecules of the optically active compound C₂₂H₂₉BrO₂, the asym-

* R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

³ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

⁴ D. T. Cromer, *Acta Cryst.*, 1965, **18**, 7.

⁵ 'X-Ray' System, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., June 1972.

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

¹ P. J. Carrol, E. L. Ghisalberti, and D. E. Ralph, *Phytochemistry*, in the press.

metric unit comprising two discrete and identical molecules of the same parity. There appear to be no significant intermolecular contacts at distances less than the van der Waals sums, and this probably accounts for the generally very high thermal motion throughout the molecule; this is most pronounced at the heavy atoms

chemistry of the ring system which is based on the tricyclo[6.2.1.0^{1,5}]undecane skeleton; three of the five chiral centres present have hydrogen atoms, that at 2 being β , those at 5 and 7 being α . At C(8), the methyl group C(8 α) is *cis* to H(7). (ii) The absolute configuration is depicted in the Figure. The same tricyclic system

TABLE 1

Atomic fractional cell (x, y, z) and thermal (10^3U \AA^2) parameters for non-hydrogen atoms, with least squares estimated standard deviations in parentheses

Atom	10^3x	10^4y	10^4z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Molecule (a) *									
C(1)	798(1)	1 812(6)	1 235(5)	48(7)	25(6)	59(7)	-1(5)	3(5)	0(5)
C(2)	796(2)	2 783(7)	1 091(6)	66(8)	52(7)	99(9)	8(6)	-6(7)	26(7)
C(2 α)	563(2)	3 121(8)	0 865(7)	134(13)	67(9)	134(12)	38(9)	10(10)	41(9)
C(3)	928(2)	2 872(8)	0 505(7)	91(10)	52(8)	156(13)	-3(7)	2(9)	44(9)
C(4)	961(2)	2 015(9)	0 210(6)	102(10)	97(10)	75(9)	-13(9)	20(8)	27(8)
C(5)	802(2)	1 396(7)	0 561(5)	58(7)	62(7)	38(6)	-10(6)	17(5)	18(6)
C(6)	838(1)	0 421(6)	0 559(5)	34(6)	44(6)	71(7)	-3(5)	-4(5)	-4(6)
C(6 α)	747(2)	0 078(9)	-0 117(5)	101(9)	82(9)	78(8)	4(9)	25(7)	-12(9)
C(6 β)	1 075(2)	0 152(8)	0 633(6)	59(8)	70(9)	105(9)	21(7)	22(7)	2(8)
C(7)	701(1)	0 052(6)	1 083(4)	66(7)	21(5)	61(6)	3(6)	3(5)	3(6)
C(8)	711(2)	0 519(6)	1 740(5)	56(7)	40(6)	56(7)	-1(6)	13(6)	-4(5)
C(8 α)	584(2)	0 037(8)	2 216(5)	74(8)	76(8)	75(8)	-18(8)	12(6)	3(8)
C(9)	935(2)	0 734(6)	2 043(5)	61(7)	50(7)	56(7)	-11(6)	-17(6)	10(6)
C(10)	990(2)	1 592(7)	1 727(5)	52(8)	64(8)	72(8)	2(6)	-24(6)	2(6)
C(11)	620(2)	1 414(6)	1 569(5)	55(7)	43(6)	54(7)	13(6)	3(6)	-7(6)
C(12)	648(2)	8 508(7)	1 153(5)	70(8)	70(9)	66(8)	-8(7)	-9(6)	-11(6)
C(13)	749(1)	7 669(6)	1 322(5)	47(7)	34(6)	64(7)	6(5)	-16(5)	-3(6)
C(14)	628(2)	6 937(7)	1 213(6)	77(9)	38(7)	122(11)	-5(7)	1(7)	4(7)
C(15)	714(2)	6 145(7)	1 383(6)	88(10)	59(8)	92(9)	-13(7)	-13(7)	-1(7)
C(16)	915(2)	6 075(7)	1 651(5)	97(9)	41(7)	46(7)	6(6)	5(6)	11(6)
C(17)	1 041(2)	6 800(7)	1 763(5)	60(8)	63(8)	55(7)	16(6)	-14(6)	4(6)
C(18)	956(2)	7 596(7)	1 598(5)	84(9)	47(7)	52(7)	5(6)	2(6)	0(6)
O(7)	786(1)	9 153(4)	1 231(3)	48(4)	40(4)	93(6)	1(3)	-13(4)	7(4)
O(12)	466(1)	8 583(5)	0 945(5)	55(5)	64(6)	161(8)	-6(4)	-35(5)	11(5)
Br	1 039.5(3)	5 000(-)	1 884.9(7)	170(1)	58(1)	83(1)	35(1)	10(1)	14(1)
Molecule (b)									
C(1)	551(1)	2 373(6)	4 374(5)	37(7)	55(7)	56(7)	1(5)	10(5)	-3(6)
C(2)	571(2)	1 403(7)	4 467(5)	41(7)	63(8)	85(9)	17(6)	4(6)	14(7)
C(2 α)	801(2)	1 034(8)	4 353(8)	93(11)	56(9)	200(16)	26(8)	31(10)	16(1)
C(3)	408(2)	1 020(7)	3 938(5)	99(9)	46(7)	62(8)	0(7)	2(7)	10(6)
C(4)	325(2)	1 735(7)	3 477(5)	81(9)	64(8)	55(7)	-16(7)	9(6)	7(6)
C(5)	495(1)	2 489(6)	3 620(5)	33(6)	40(6)	54(7)	-19(5)	-10(5)	13(5)
C(6)	431(1)	3 385(6)	3 393(4)	40(6)	56(7)	49(7)	-3(6)	10(5)	7(6)
C(6 α)	471(2)	3 475(7)	2 654(5)	61(7)	65(8)	57(2)	1(7)	6(6)	19(6)
C(6 β)	194(1)	3 631(6)	3 439(5)	32(6)	66(8)	58(7)	1(5)	-8(5)	5(6)
C(7)	590(2)	4 015(6)	3 782(5)	63(7)	20(6)	75(8)	13(5)	-6(6)	-6(6)
C(8)	644(1)	3 850(7)	4 515(4)	41(6)	68(7)	45(6)	6(6)	9(5)	-5(7)
C(8 α)	797(2)	4 560(7)	4 803(5)	60(8)	79(9)	68(8)	-3(7)	-18(7)	-15(7)
C(9)	450(2)	3 711(8)	4 911(5)	48(7)	93(9)	46(6)	28(7)	8(5)	13(7)
C(10)	389(2)	2 760(8)	4 819(5)	47(7)	98(9)	57(8)	21(7)	19(6)	4(7)
C(11)	741(1)	2 946(6)	4 553(4)	39(7)	59(7)	39(6)	10(5)	-13(5)	-2(5)
C(12)	587(2)	5 540(7)	3 452(5)	50(7)	65(8)	77(8)	-22(6)	22(6)	7(6)
C(13)	455(2)	6 325(6)	3 415(5)	56(7)	40(6)	67(8)	5(6)	-1(6)	-3(6)
C(14)	534(2)	7 037(7)	3 128(6)	75(9)	46(7)	103(9)	-11(6)	-15(7)	19(7)
C(15)	421(2)	7 797(8)	3 087(6)	110(11)	62(8)	85(9)	-33(8)	-1(8)	12(7)
C(16)	231(2)	7 814(7)	3 327(5)	124(11)	36(7)	63(8)	-11(7)	-10(7)	2(6)
C(17)	140(2)	7 118(7)	3 597(5)	62(8)	61(8)	70(8)	4(6)	-8(6)	8(6)
C(18)	257(2)	6 361(7)	3 647(5)	44(7)	61(7)	58(7)	-1(6)	-15(6)	5(6)
O(7)	487(1)	4 900(5)	3 729(3)	50(4)	70(5)	74(5)	-2(4)	15(4)	-1(5)
O(12)	756(1)	5 495(5)	3 273(5)	66(6)	88(6)	142(8)	2(5)	51(5)	24(6)
Br	066.9(3)	8 854(1)	3 256.3(8)	166(1)	60(1)	125(1)	30(1)	-47(1)	0(1)

* Molecule (a) straddles the cell boundary and is given here as two fragments; the molecular geometry in Table 2 is that of a connected set.

themselves and probably accounts for the poor accuracy of the bromine positions in spite of the low R , as well as the apparent distortions within the benzene ring.

The structure determination has elucidated the following points arising out of the molecular geometry and its associated chemistry. (i) The nature and stereo-

chemistry of the ring system which is based on the tricyclo[6.2.1.0^{1,5}]undecane skeleton; three of the five chiral centres present have hydrogen atoms, that at 2 being β , those at 5 and 7 being α . (ii) The absolute configuration is depicted in the Figure. The same tricyclic system

* R. M. Coates, R. F. Farney, S. M. Johnson, and I. C. Paul, *Chem. Comm.*, 1969, 999.

TABLE 2

Interatomic distances (Å) and angles (°) with least squares estimated standard deviations in parentheses. Values for molecule (b) follow those for molecule (a)

C(1)—C(2)	1.54(1), 1.53(1)
C(1)—C(5)	1.53(1), 1.56(1)
C(1)—C(10)	1.54(1), 1.55(1)
C(1)—C(11)	1.51(1), 1.52(1)
C(2)—C(2 α)	1.60(2), 1.60(2)
C(2)—C(3)	1.53(2), 1.55(1)
C(3)—C(4)	1.49(2), 1.52(1)
C(4)—C(5)	1.61(2), 1.60(1)
C(5)—C(6)	1.53(1), 1.51(1)
C(6)—C(6 α)	1.54(1), 1.56(1)
C(6)—C(6 β)	1.55(1), 1.56(1)
C(6)—C(7)	1.55(1), 1.57(1)
C(7)—O(7)	1.52(1), 1.53(1)
C(7)—C(8)	1.53(1), 1.53(1)
C(8)—C(8 α)	1.52(2), 1.55(1)
C(8)—C(9)	1.54(1), 1.55(1)
C(8)—C(11)	1.54(1), 1.53(1)
C(9)—C(10)	1.54(1), 1.54(2)
O(7)—C(12)	1.33(1), 1.34(1)
C(12)—O(12)	1.20(1), 1.16(1)
C(12)—C(13)	1.48(1), 1.48(1)
C(13)—C(14)	1.38(1), 1.37(2)
C(14)—C(15)	1.38(2), 1.38(2)
C(15)—C(16)	1.35(2), 1.34(2)
C(16)—Br	1.89(1), 1.92(2)
C(16)—C(17)	1.39(1), 1.37(2)
C(17)—C(18)	1.38(1), 1.39(1)
C(13)—C(18)	1.39(1), 1.38(1)
C(13)—C(14)—C(15)	119.7(10), 120.6(11)
C(14)—C(15)—C(16)	120.9(11), 118.2(11)
C(14)—C(13)—C(18)	119.3(9), 119.7(10)
C(15)—C(16)—C(17)	120.6(10), 123.9(11)
C(16)—C(17)—C(18)	119.0(9), 117.4(10)
C(13)—C(18)—C(17)	120.5(9), 120.1(10)
C(15)—C(16)—Br	122.1(8), 119.2(8)
C(17)—C(16)—Br	117.3(8), 116.8(9)
C(5)—C(1)—C(11)	108.1(8), 105.8(8)
C(5)—C(1)—C(10)	114.8(8), 115.8(8)
C(10)—C(1)—C(11)	101.0(8), 100.5(8)
C(2)—C(1)—C(5)	104.1(8), 104.2(8)
C(2)—C(1)—C(10)	109.5(8), 111.4(9)
C(2)—C(1)—C(11)	119.9(8), 119.6(8)
C(1)—C(2)—C(2 α)	111.7(9), 113.9(9)
C(1)—C(2)—C(3)	104.2(9), 104.4(8)
C(2 α)—C(2)—C(3)	107.4(10), 108.6(9)
C(2)—C(3)—C(4)	110.1(10), 108.9(9)
C(3)—C(4)—C(5)	103.9(9), 103.4(8)
C(4)—C(5)—C(6)	119.3(9), 117.3(7)
C(1)—C(5)—C(4)	102.2(8), 100.6(7)
C(1)—C(5)—C(6)	115.9(8), 116.1(8)
C(5)—C(6)—C(6 α)	107.4(8), 108.5(8)
C(5)—C(6)—C(6 β)	114.2(8), 116.3(8)
C(5)—C(6)—C(7)	105.7(8), 105.9(7)
C(6 α)—C(6)—C(6 β)	106.0(9), 106.2(7)
C(6 α)—C(6)—C(7)	107.7(8), 106.3(8)
C(6 β)—C(6)—C(7)	115.4(8), 113.3(8)
C(6)—C(7)—O(7)	105.7(7), 105.7(7)
C(6)—C(7)—C(8)	117.0(8), 117.8(8)
O(7)—C(7)—C(8)	106.1(7), 106.0(7)
C(7)—C(8)—C(8 α)	110.4(8), 109.1(8)
C(7)—C(8)—C(9)	114.9(8), 115.0(7)
C(7)—C(8)—C(11)	104.3(8), 104.7(8)
C(8 α)—C(8)—C(9)	112.0(8), 113.5(8)
C(8 α)—C(8)—C(11)	112.5(9), 113.5(7)
C(9)—C(8)—C(11)	102.2(8), 100.4(8)
C(8)—C(11)—C(1)	101.1(8), 102.7(7)
C(8)—C(9)—C(10)	104.7(8), 105.8(9)
C(9)—C(10)—C(1)	105.9(8), 106.0(8)
C(7)—O(7)—C(12)	117.1(7), 118.8(7)
O(7)—C(12)—O(12)	124.7(10), 125.2(10)
O(7)—C(12)—C(13)	111.9(8), 110.3(9)
O(12)—C(12)—C(13)	123.4(10), 124.4(10)
C(12)—C(13)—C(14)	117.9(9), 117.5(10)
C(12)—C(13)—C(18)	122.7(9), 122.8(9)

TABLE 3

Torsion angles within the alicyclic (non-hydrogen) skeletons; values for molecule (b) follow those for molecule (a)

C(10)—C(1)—C(2)—C(2 α)	154.6, 149.4
C(11)—C(1)—C(2)—C(2 α)	38.7, 32.7
C(10)—C(1)—C(2)—C(3)	-89.9, -92.3
C(11)—C(1)—C(2)—C(3)	154.3, 151.1
C(5)—C(1)—C(2)—C(2 α)	-82.2, -85.1
C(5)—C(1)—C(2)—C(3)	33.4, 33.3
C(1)—C(2)—C(3)—C(4)	-13.4, -9.9
C(2 α)—C(2)—C(3)—C(4)	105.2, 112.0
C(2)—C(3)—C(4)—C(5)	-10.8, -16.7
C(3)—C(4)—C(5)—C(6)	160.4, 162.9
C(3)—C(4)—C(5)—C(1)	31.1, 36.0
C(6)—C(7)—C(8)—C(8 α)	-175.3, -178.0
C(6)—C(7)—C(8)—C(9)	-47.3, -49.1
C(6)—C(7)—C(8)—C(11)	63.7, 60.1
C(7)—C(8)—C(9)—C(10)	-85.2, -83.1
C(8 α)—C(8)—C(9)—C(10)	147.6, 150.2
C(11)—C(8)—C(9)—C(10)	27.0, 28.7
C(8)—C(11)—C(1)—C(5)	-72.9, -73.4
C(8)—C(11)—C(1)—C(2)	168.3, 169.6
C(8)—C(11)—C(1)—C(10)	48.0, 47.4
C(9)—C(8)—C(11)—C(1)	47.2, 47.6
C(4)—C(5)—C(1)—C(2)	39.6, 42.9
C(4)—C(5)—C(1)—C(10)	-80.1, -79.8
C(4)—C(5)—C(1)—C(11)	168.0, 169.9
C(6)—C(5)—C(1)—C(2)	171.0, 170.6
C(6)—C(5)—C(1)—C(10)	51.4, 47.8
C(6)—C(5)—C(1)—C(11)	-60.5, -62.5
C(1)—C(5)—C(6)—C(6 β)	85.9, 83.1
C(4)—C(5)—C(6)—C(7)	-164.9, -162.5
C(1)—C(5)—C(6)—C(7)	-42.1, -43.6
C(4)—C(5)—C(6)—C(6 α)	80.3, 83.8
C(4)—C(5)—C(6)—C(6 β)	-37.0, -35.7
C(1)—C(5)—C(6)—C(6 α)	-156.8, -157.4
C(6 α)—C(6)—C(7)—C(8)	160.0, 159.1
C(6 β)—C(6)—C(7)—C(8)	-81.9, -84.7
C(5)—C(6)—C(7)—C(8)	45.4, 43.9
C(8)—C(9)—C(10)—C(1)	2.3, -0.3
C(9)—C(10)—C(1)—C(2)	-158.6, -156.3
C(9)—C(10)—C(1)—C(5)	84.8, 84.8
C(9)—C(10)—C(1)—C(11)	-31.2, -28.6
C(7)—C(8)—C(11)—C(1)	-72.8, -71.9
C(8 α)—C(8)—C(11)—C(1)	167.5, 169.1

TABLE 4

Equations of least-squares planes in the form $pX + qY + rZ = s$; the orthogonal (Å) frame is defined by $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$. Atom deviations (Å) are in square brackets; σ (Å) is the estimated standard deviation of the defining atoms. Values for molecule (b) follow those for molecule (a)

$10^4 p$	$10^4 q$	$10^4 r$	s	σ	χ^2
Plane (i): C(12)—C(18), O(7), O(12) Br					
-3 767	0 924	9 217	1 901	0.04	125
3 373	2 833	8 978	9 802	0.01	19.3
[Br 0.01, 0.00; C(12) 0.02, 0.00; C(13) -0.01, 0.00; C(14) -0.04, -0.03; C(15) -0.03, -0.01; C(16) 0.00, 0.02; C(17) 0.03, 0.00; C(18) 0.02, 0.00; O(7) -0.06, -0.01; O(12) 0.06, 0.02]					
Plane (ii): C(1)—(5)					
8 391	-1 678	5 174	4 639	0.20	1 197
-8 369	2 574	4 830	2 759	0.22	1 774
[C(1) 0.24, 0.26; C(2) -0.15, -0.14; C(3) 0.00, -0.03; C(4) 0.13, 0.17; C(5) -0.23, -0.26; C(6) 0.21, 0.18; C(10) 1.76, 1.77; C(11) -0.30, -0.32; C(2 α) -1.68, -1.63]					
Plane (iii): C(1), C(8)—(11)					
-2 685	4 981	8 245	2 439	0.24	2 440
3 978	-2 001	9 160	8 608	0.24	2 365
[C(1) -0.26, -0.24; C(8) -0.24, -0.24; C(9) 0.07, 0.09; C(10) 0.10, 0.08; C(11) 0.32, 0.32; C(2) 0.25, 0.27; C(5) -1.75, -1.76; C(8 α) 0.43, 0.39; C(7) -1.72, -1.74]					

of the zizane series)⁷ and this is in general agreement with the chemistries of the two systems.

The following features arise out of the nature of the ring fusion. (i) The six-membered ring is a chair [H(5 α , 7 α , 11 α) all axial], somewhat distorted by the ethano-bridge C(1)–C(8); the internal ring angles range from *ca.* 102 to 117°. The junctions to the five-membered ring at C(1) and C(5) are *trans*.

(ii) The five-membered ring formed by the ethano-bridge has the usual conformation with C(1), C(8), C(9), and C(10) closely planar and C(11) deviating appreciably,

⁷ R. Sakuma and A. Yoshikoshi, *Chem. Comm.*, 1968, 41; F. Kido, H. Uda, and A. Yoshikoshi, *J.C.S. Perkin I*, 1972, 1755.

with overall approximate *m* symmetry. The other five-membered ring, however, is not describable in terms of a plane and has an unusual symmetry very close to C_2 with an approximate two-fold axis passing through C(3).

(iii) The ¹H n.m.r. spectrum of the alcohol for pyridine rather than CCl₄ solution shows a deshielding effect on each of the three methyl groups C(6 α), C(6 β), and C(8 α); the shifts are 0.13, 0.16, 0.19 p.p.m. and may be due to the proximity of O(7).

The phenyl group of molecule (a) exhibits an appreciable twist relative to its associated carboxylate. There are no unusually short intermolecular contacts.

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