Structure and Absolute Configuration of α-Pompene. II. An X-Ray Analysis of the Mono *p*-Bromobenzoate of the Diol Derived from α-Pompene

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The mono *p*-bromobenzoate of the diol derived from α-pompene has been studied by X-ray crystal structure analysis and determined to be 9-*p*-bromobenzoxy-8-hydroxy-1,2,6,8-tetramethyltricyclo[5.3.1.$0^{2,6}$]undecane. The crystals are of the orthorhombic space group $P2_12_12_1$, $a=46.53(2)$, $b=12.20(2)$, $c=7.39(2)$ Å, $Z=8$, and hence there are two independent molecules per asymmetric unit. The structure was solved by the heavy-atom methods, and refined by block-diagonal least-squares calculations to a final R value of 0.103 for 2493 observed reflections. The structures of the two independent molecules in the asymmetric unit are quite similar. Both molecules contain a tricyclo[5.3.1.$0^{2,6}$]undecane ring in which three fused rings (cyclohexane, cyclopentane, and cyclopentane) are present. The overall configuration of these three fused rings can be described as a "*cis*" type. The conformation of the cyclohexane ring is of a chair form, and the two cyclopentane rings exhibit envelope forms. Based on the anomalous X-ray dispersion effect of the bromine atoms, the absolute configuration of the title compound was also determined.

(+)-α-Pompene, $C_{15}H_{24}$, is a novel tricyclic sesquiterpene hydrocarbon which was isolated from the extract of a liverwort, *Bazzania pompeana* (Lac.) Mitt. together with (−)-β-pompene. We have previously assigned the structure (I) for (+)-α-pompene on the basis of the chemical and spectral evidence.[1] For the purpose of confirming this structure, α-pompene was converted to a diol. Its mono *p*-bromobenzoate was prepared for examination by X-ray crystallographic analysis. The conclusion was that the structures of (+)-α- and (−)-β-pompene should be represented by 1,2,6,8-tetramethyltricyclo[5.3.1.$0^{2,6}$]undec-8-ene (II) and 1,2,6,8-tetramethyltricyclo[5.3.1.$0^{2,6}$]undec-8(15)-ene (III), respectively.[2] A portion of this result has already been reported briefly, together with the absolute configurations of the hydrocarbons, which were determined by the CD measurement.[3] We report here the detailed results of the X-ray crystal structure analysis of α-pompene diol mono *p*-bromobenzoate.

Experimental

The crystals of mono *p*-bromobenzoate, $C_{22}H_{29}O_3Br$, mp 79—80 °C were recrystallized from a hexane–EtOAc (4: 1) mixture at room temperature.[3] The colorless crystals thus obtained were well-formed needles elongated along the c-axis. Crystal data are as follows: $C_{22}H_{29}O_3Br$, $M=421.4$, Orthorhombic, $a=46.53(2)$, $b=12.20(2)$, $c=7.39(2)$ Å, $U=4195$ Å^3, $D_m=1.31$ (by flotation in $ZnCl_2$ solution), $Z=8$, $D_c=1.33$ g/cm^3, $F(000)=1760$; Ni $K\alpha$ radiation ($\lambda=1.6591$ Å), $\mu=38.2$ cm^{-1}. The space group is shown to be $P2_12_12_1$ (D_2^4) from the following systematic absences: $h00$ when $h=2n+1$, $0k0$ when $k=2n+1$, and $00l$ when $l=2n+1$. The unit-cell dimensions were evaluated from the least-squares refinement of the $hk0$, $h0l$, and $0kl$ reflection data recorded on Weissenberg photographs calibrated with a sodium chloride crystal. The data for the intensity measurements were recorded by equi-inclination multiple-film Weissenberg photographs (Ni $K\alpha$ radiation) of the $hk0$-$hk5$ and $h0l$ reciprocal lattice levels. The intensity data obtained (maximum $\sin\theta/\lambda=0.55$) were estimated visually by the comparison with a calibrated intensity scale. Spot-shape and the usual Lorentz and polarization corrections were applied, and 2840 independent observed structure amplitudes were obtained. No correction was made for absorption ($\mu r=0.5$).

Solution and Refinement of the Structure

The structure was solved by the heavy-atom methods. Initial coordinates for the two independent bromine atoms were derived from the three-dimensional Patterson map. The subsequent electron density syntheses, though complicated in the first step by the false inversion center, finally gave the non-hydrogen atom skeleton of both molecules.

This model was refined by several cycles of the block-diagonal least-squares adjustment of the positional and the isotropic thermal parameters using the HBLS program.[4] Cruickshank's weighting scheme was used, in which $W=1/(A+B|F_o|+C|F_o|^2)$, and $A=5.0$, $B=1.0$, and $C=0.024$.[5] The scattering factors from the "International Table" were used.[6] The final difference electron density map showed no spurious peak. However, it was difficult to estimate the hydrogen-atom positions clearly. Hydrogen atoms, except for methyl groups, were therefore located by assuming the C–H bond length of 1.08 Å and the tetrahedral angle for each carbon atom. Contributions for hydrogen atoms with fixed position and isotropic thermal factor $B=4.5$ were included in further least-squares iterations, during which the non-hydrogen atoms were allowed to assume anisotropic temperature factors. The final R value was 0.103 for 2493 non-zero reflections.

In the final stage of the refinements the absolute configuration of the molecule was determined by the anomalous dispersion method.[7] In order to estimate the differences between $I_o(hkl)$ and $I_o(\bar{h}\bar{k}\bar{l})$ values, both intensities were measured visually from the Weissenberg

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Table 1. Determination of the absolute configuration (Ni $K\alpha$ radiation)

h	k	l	Calcd $F^2(hkl)$	Calcd $F^2(\bar{h}\bar{k}\bar{l})$	Obsd $I(hkl)$ vs $I(\bar{h}\bar{k}\bar{l})$
11	2	1	160	230	<
1	4	1	150	202	≪
8	4	1	343	259	>
1	5	1	430	360	>
7	6	1	213	180	≫
15	1	2	97	128	<
18	1	2	88	114	≪
13	2	2	287	242	>
1	3	2	14	5	>
10	1	3	242	288	<
18	1	3	52	31	≫
6	3	3	120	93	>
9	3	3	134	104	>
3	5	3	132	109	>
2	1	5	69	53	≫

photographs rotated around the c-axis, as taken with Ni $K\alpha$ radiation. Structure factors were calculated for all the hkl and $\bar{h}\bar{k}\bar{l}$ reflections, using an atomic scattering factor for the bromine atom of the form $f_{Br}=f_{Br}+\Delta f'_{Br}+i\Delta f''_{Br}$, where $\Delta f'_{Br}=-0.86$ and $\Delta f''_{Br}=1.63$.[8] The results are summarized in Table 1. These results also indicate that the parameters of Table 2 represent the true absolute configuration. The table of observed and calculated structure factors is kept as Document No. 7803 at the Chemical Society of Japan.

Result and Discussion

The final atomic coordinates and anisotropic thermal parameters ($\times 10^4$) are listed in Table 2. The interatomic distances and valency angles, with the estimated standard deviations in parentheses, are also listed in Table 3. The atomic arrangement in the two crystallographically independent molecules of α-pompene diol *p*-bromobenzoate viewed along the c-axis is shown in Fig. 1. The numbering scheme of the atoms in this figure agrees with the conventional chemical sequence employed in the chemical formula (IVb). The two molecules have very similar conformations; the skeleton of each molecule consists of three rings: cyclohexane and the two cyclopentanes. For purposes of comparison, the values for the two molecules of the asymmetric unit are labeled A and B respectively, and those for the latter data are shown in square brackets. From the above results, the structure of α-pompene diol can be shown by the chemical formula 1,2,6,8-tetramethyltricyclo[5.3.1.$0^{2,6}$]undecan-8,9-diol, with the stereochemistry (IVa) and the overall molecular conformation (IVb). Therefore, the structure assigned previously to α-pompene should be revised to be 1,2,6,8-tetramethyltricyclo[5.3.1.$0^{2,6}$]undec-8-ene, while that of β-pompene is 1,2,6,8-tetramethyltricyclo[5.3.1.$0^{2,6}$]undec-8(15)-ene. The absolute configurations of their compounds are presented by stereostructures (II) and (III). The equations of planes and the displacements of the atoms from the mean planes are listed in Table 4.

Table 2. Positional and thermal parameters of atoms (e.s.d.'s in parentheses)

(a) Fractional co-ordinates.

Molecule A	X	Y	Z	Molecule B	X	Y	Z
Br	0.4039(1)	0.5832(3)	0.4267(6)	Br	0.3320(1)	0.8978(3)	0.9478(6)
O(1)	0.2650(3)	0.7473(13)	1.1373(21)	O(1)	0.4828(3)	0.8566(16)	0.3035(24)
O(2)	0.2749(3)	0.7147(12)	0.7900(20)	O(2)	0.4681(3)	0.8406(16)	0.6458(22)
O(3)	0.2611(3)	0.7143(12)	0.5017(22)	O(3)	0.4781(3)	0.8062(14)	0.9398(23)
C(1)	0.2110(5)	0.9000(20)	0.9287(36)	C(1)	0.5445(4)	0.9244(19)	0.5397(35)
C(2)	0.1834(4)	0.8359(17)	0.8714(38)	C(2)	0.5643(4)	0.8313(21)	0.6119(41)
C(3)	0.1812(5)	0.7933(21)	0.6756(43)	C(3)	0.5600(5)	0.7822(24)	0.7925(37)
C(4)	0.1671(6)	0.6765(26)	0.7008(56)	C(4)	0.5644(7)	0.6552(22)	0.7672(53)
C(5)	0.1828(5)	0.6267(23)	0.8600(38)	C(5)	0.5472(7)	0.6297(24)	0.6052(44)
C(6)	0.1845(4)	0.7212(20)	0.9947(35)	C(6)	0.5540(4)	0.7216(22)	0.4724(38)
C(7)	0.2133(5)	0.7425(16)	1.1114(41)	C(7)	0.5321(4)	0.7800(17)	0.3390(35)
C(8)	0.2423(4)	0.7013(17)	1.0325(36)	C(8)	0.4997(4)	0.7811(18)	0.4077(35)
C(9)	0.2449(4)	0.7326(16)	0.8482(27)	C(9)	0.4989(3)	0.8166(16)	0.5998(40)
C(10)	0.2386(4)	0.8582(19)	0.8281(34)	C(10)	0.5151(5)	0.9291(17)	0.6239(33)
C(11)	0.2147(4)	0.8654(19)	1.1274(37)	C(11)	0.5407(5)	0.8987(17)	0.3405(32)
C(12)	0.2095(5)	1.0264(14)	0.9108(44)	C(12)	0.5580(5)	1.0453(19)	0.5750(50)
C(13)	0.1554(5)	0.9053(22)	0.9087(55)	C(13)	0.5975(5)	0.8552(36)	0.5830(60)
C(14)	0.1601(5)	0.7119(21)	1.1333(42)	C(14)	0.5779(5)	0.6779(23)	0.3402(43)
C(15)	0.2455(5)	0.5692(21)	1.0487(44)	C(15)	0.4836(5)	0.6575(26)	0.3982(55)
C(16)	0.2794(4)	0.7024(14)	0.6168(29)	C(16)	0.4615(4)	0.8310(20)	0.8151(34)
C(17)	0.3108(4)	0.6761(17)	0.5690(33)	C(17)	0.4288(5)	0.8434(15)	0.8457(39)
C(18)	0.3195(4)	0.6894(18)	0.4013(34)	C(18)	0.4179(5)	0.8454(19)	1.0211(33)
C(19)	0.3482(4)	0.6600(17)	0.3599(40)	C(19)	0.3890(4)	0.8614(23)	1.0517(41)
C(20)	0.3660(4)	0.6236(21)	0.4827(40)	C(20)	0.3710(5)	0.8760(20)	0.9108(42)
C(21)	0.3574(4)	0.6121(21)	0.6563(41)	C(21)	0.3822(5)	0.8795(29)	0.7321(44)
C(22)	0.3287(4)	0.6404(23)	0.7094(33)	C(22)	0.4115(5)	0.8658(20)	0.6987(39)

(b) Anisotropic temperature factors ($\times 10^4$) expressed in the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Molecule A	$\beta^{a)}{}_{11}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	53(1)	190(4)	471(10)	18(1)	12(2)	61(12)
O(1)	49(7)	130(15)	175(40)	−9(5)	−14(9)	−27(39)
O(2)	45(6)	113(13)	152(36)	0(5)	2(7)	12(38)
O(3)	41(6)	110(13)	232(41)	12(5)	8(8)	17(40)
C(1)	56(11)	108(22)	247(67)	6(8)	6(13)	1(70)
C(2)	38(9)	68(17)	364(75)	−2(6)	−4(13)	33(60)
C(3)	75(14)	89(21)	356(84)	15(9)	13(18)	−32(73)
C(4)	85(17)	142(30)	559(122)	−26(12)	3(24)	−317(106)
C(5)	61(12)	140(27)	267(72)	−21(10)	−10(15)	−20(76)
C(6)	49(10)	111(22)	236(66)	2(8)	11(13)	107(63)
C(7)	76(14)	47(16)	318(76)	−2(7)	6(16)	27(56)
C(8)	57(11)	61(16)	276(68)	4(7)	4(14)	−84(55)
C(9)	40(8)	74(16)	104(51)	−4(6)	4(9)	15(45)
C(10)	42(9)	94(20)	263(65)	−11(7)	−2(13)	34(6)
C(11)	56(11)	93(20)	262(71)	0(8)	0(13)	15(62)
C(12)	92(15)	13(14)	431(88)	−3(7)	−7(19)	71(57)
C(13)	51(11)	106(24)	651(122)	−1(8)	−3(20)	123(108)
C(14)	64(12)	96(2)	379(88)	−23(9)	38(17)	−29(72)
C(15)	63(12)	91(21)	432(89)	13(8)	−17(17)	60(79)
C(16)	47(9)	44(14)	159(52)	4(6)	−4(10)	23(44)
C(17)	44(9)	80(17)	206(58)	6(6)	−16(12)	−39(55)
C(18)	35(8)	96(19)	241(64)	5(6)	−5(11)	−37(59)
C(19)	43(9)	56(16)	418(83)	−8(6)	9(14)	119(64)
C(20)	48(10)	118(24)	348(79)	9(8)	6(14)	−156(75)
C(21)	44(10)	115(23)	386(80)	13(8)	−30(15)	20(77)
C(22)	36(9)	164(27)	176(59)	11(8)	−3(11)	139(67)

Molecule B	$\beta^{a)}{}_{11}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	59(1)	161(3)	534(11)	10(1)	10(2)	−182(11)
O(1)	60(8)	160(18)	237(45)	6(7)	6(10)	107(51)
O(2)	54(7)	170(19)	168(39)	10(6)	−1(8)	−17(47)
O(3)	46(7)	132(15)	206(41)	−4(5)	−18(8)	25(44)
C(1)	30(8)	102(20)	321(67)	−3(6)	14(12)	81(67)
C(2)	34(9)	122(23)	385(82)	1(4)	−5(14)	165(76)
C(3)	76(14)	137(26)	214(70)	−4(10)	−26(16)	−102(77)
C(4)	121(22)	86(23)	496(112)	−26(11)	−32(26)	175(91)
C(5)	120(21)	118(26)	315(86)	11(12)	22(23)	110(86)
C(6)	50(10)	137(26)	295(75)	8(8)	−30(13)	−206(77)
C(7)	35(8)	68(16)	302(66)	−4(6)	−6(12)	−10(57)
C(8)	55(10)	99(18)	63(51)	−11(7)	1(10)	−107(50)
C(9)	29(8)	52(15)	460(83)	−4(5)	11(14)	53(63)
C(10)	72(12)	64(17)	199(60)	5(8)	0(13)	6(54)
C(11)	81(13)	60(17)	194(59)	−10(8)	−14(14)	−24(53)
C(12)	68(13)	73(20)	523(100)	−24(8)	−14(20)	58(84)
C(13)	30(10)	285(50)	625(129)	−16(11)	−26(19)	112(157)
C(14)	69(13)	137(27)	333(82)	30(10)	25(17)	−22(80)
C(15)	47(11)	150(29)	598(119)	−14(10)	−1(20)	−170(112)
C(16)	40(9)	125(23)	218(62)	−4(7)	−16(12)	−136(63)
C(17)	73(12)	27(14)	357(76)	−19(7)	22(16)	−20(55)
C(18)	75(13)	85(19)	180(63)	−8(8)	13(14)	16(57)
C(19)	44(10)	147(26)	332(79)	−11(9)	15(15)	32(85)
C(20)	63(12)	98(22)	343(78)	11(8)	−1(16)	−37(75)
C(21)	56(13)	185(35)	398(96)	2(10)	−36(18)	−132(97)
C(22)	77(13)	88(20)	260(71)	13(9)	2(16)	9(65)

a) All values for β_{11} are shown in the scale factor $\times 10^5$.

(c) Calculated co-ordinates and the assigned isotropic temperature factor for hydrogen atoms.

Molecule A	X	Y	Z	B
H(3a)	0.167	0.846	0.593	4.5
H(3b)	0.202	0.788	0.612	4.5
H(4a)	0.144	0.678	0.279	4.5
H(4b)	0.170	0.623	0.581	4.5
H(5a)	0.171	0.557	0.921	4.5
H(5b)	0.204	0.597	0.822	4.5
H(7)	0.211	0.693	1.238	4.5
H(9)	0.230	0.683	0.766	4.5
H(10a)	0.257	0.905	0.873	4.5
H(10b)	0.236	0.877	0.680	4.5
H(11a)	0.235	0.895	1.183	4.5
H(11b)	0.198	0.901	1.125	4.5
H(18)	0.305	0.720	0.292	4.5
H(19)	0.357	0.672	0.222	4.5
H(21)	0.372	0.581	0.760	4.5
H(22)	0.321	0.630	0.845	4.5

Molecule B	X	Y	Z	B
H(3a)	0.575	0.818	0.889	4.5
H(3b)	0.538	0.801	0.842	4.5
H(4a)	0.587	0.632	0.752	4.5
H(4b)	0.557	0.607	0.887	4.5
H(5a)	0.553	0.550	0.544	4.5
H(5b)	0.524	0.627	0.633	4.5
H(7)	0.533	0.735	0.206	4.5
H(9)	0.510	0.775	0.713	4.5
H(10a)	0.503	0.995	0.560	4.5
H(10b)	0.518	0.950	0.767	4.5
H(11a)	0.524	0.950	0.279	4.5
H(11b)	0.561	0.913	0.266	4.5
H(18)	0.433	0.831	1.135	4.5
H(19)	0.380	0.869	1.191	4.5
H(21)	0.367	0.893	0.622	4.5
H(22)	0.420	0.868	0.561	4.5

The tricyclo[5.3.1.$0^{2,6}$]undecane framework of the α-pompene derivative has a crowded "*cis*" configuration.[9] In relation to the chemical formula, tricyclo-[5.3.1.$0^{2,6}$]undecane, this new framework is in agreement with that of α-caryophyllene alcohol (Va).[10] However, the configurations of the bicyclo[3.3.0]octane fragment in the two molecules are completely different. The α-caryophyllene alcohol framework has a strain free "*trans*" configuration (Vb).[9]

The cyclohexane ring, (C(7), C(8), C(9), C(10), C(1), and C(11)), in both A and B molecules adopts a chair conformation. As shown in Fig. 1, the two oxygen atoms which belong to the diol groups occupy the axial position for the O(1) atom and the equatorial position

TABLE 3. BOND LENGTHS AND BOND ANGLES (e.s.d.'s IN PARENTHESES)
The values of molecule B are shown in square brackets.

(a) Bond lengths [Å]

Br	– C(20)	1.88(3) [1.85(3)]	O(1)	– C(8)	1.42(3) [1.44(3)]
O(2)	– C(9)	1.48(3) [1.50(4)]	O(2)	– C(16)	1.31(3) [1.29(3)]
O(3)	– C(16)	1.21(3) [1.24(3)]	C(1)	– C(2)	1.56(4) [1.56(4)]
C(1)	– C(10)	1.57(4) [1.51(4)]	C(1)	– C(11)	1.54(4) [1.52(4)]
C(1)	– C(12)	1.55(4) [1.62(5)]	C(2)	– C(3)	1.54(4) [1.48(4)]
C(2)	– C(6)	1.67(4) [1.76(4)]	C(2)	– C(13)	1.58(5) [1.59(5)]
C(3)	– C(4)	1.58(5) [1.57(5)]	C(4)	– C(5)	1.51(5) [1.47(5)]
C(5)	– C(6)	1.53(4) [1.52(4)]	C(6)	– C(7)	1.61(4) [1.59(4)]
C(6)	– C(14)	1.54(4) [1.58(4)]	C(7)	– C(8)	1.56(4) [1.59(3)]
C(7)	– C(11)	1.51(4) [1.50(4)]	C(8)	– C(9)	1.42(3) [1.48(4)]
C(8)	– C(15)	1.62(4) [1.69(5)]	C(9)	– C(10)	1.57(3) [1.58(4)]
C(16)	– C(17)	1.53(3) [1.55(4)]	C(17)	– C(18)	1.31(4) [1.39(4)]
C(17)	– C(22)	1.40(4) [1.38(4)]	C(18)	– C(19)	1.41(4) [1.38(4)]
C(19)	– C(20)	1.31(4) [1.35(4)]	C(20)	– C(21)	1.35(4) [1.40(5)]
C(21)	– C(22)	1.44(4) [1.40(5)]			

(b) Bond angles [°]

C(9) – O(2) – C(16)	117.0(17)	[115.4(21)]	O(1) – C(8) – C(7)	108.2(21)	[110.8(18)]
C(2) – C(1) – C(10)	112.6(21)	[115.1(21)]	O(1) – C(8) – C(9)	110.7(21)	[108.2(20)]
C(2) – C(1) – C(11)	102.4(21)	[104.5(21)]	O(1) – C(8) – C(15)	106.5(21)	[107.9(21)]
C(2) – C(1) – C(12)	115.8(23)	[112.2(20)]	C(7) – C(8) – C(9)	110.2(22)	[109.5(20)]
C(10) – C(1) – C(11)	105.9(21)	[107.8(21)]	C(7) – C(8) – C(15)	111.8(23)	[113.6(21)]
C(10) – C(1) – C(12)	108.7(22)	[104.6(22)]	C(9) – C(8) – C(15)	109.3(21)	[106.8(22)]
C(11) – C(1) – C(12)	111.0(23)	[112.9(22)]	O(2) – C(9) – C(8)	108.7(18)	[107.5(21)]
C(1) – C(2) – C(3)	118.6(23)	[121.7(25)]	O(2) – C(9) – C(10)	107.1(17)	[105.1(21)]
C(1) – C(2) – C(6)	104.1(21)	[101.1(21)]	C(8) – C(9) – C(10)	109.8(19)	[110.4(22)]
C(1) – C(2) – C(13)	111.4(24)	[113.4(26)]	C(1) – C(10) – C(9)	115.1(20)	[110.9(21)]
C(3) – C(2) – C(6)	103.4(22)	[100.7(22)]	C(1) – C(11) – C(7)	101.1(22)	[103.7(20)]
C(3) – C(2) – C(13)	106.9(25)	[109.1(27)]	O(2) – C(16) – O(3)	124.2(20)	[126.2(23)]
C(6) – C(2) – C(13)	112.4(24)	[109.1(25)]	O(2) – C(16) – C(17)	113.7(18)	[111.6(22)]
C(2) – C(3) – C(4)	102.8(26)	[105.9(26)]	O(3) – C(16) – C(17)	122.0(20)	[122.0(22)]
C(3) – C(4) – C(5)	104.7(29)	[103.5(29)]	C(16) – C(17) – C(18)	119.0(22)	[119.8(23)]
C(4) – C(5) – C(6)	103.2(25)	[104.9(27)]	C(16) – C(17) – C(22)	117.3(21)	[118.6(24)]
C(2) – C(6) – C(5)	106.0(21)	[103.8(22)]	C(18) – C(17) – C(22)	123.6(24)	[121.1(25)]
C(2) – C(6) – C(7)	100.6(20)	[101.4(20)]	C(17) – C(18) – C(19)	117.7(24)	[120.8(25)]
C(2) – C(6) – C(14)	113.7(22)	[115.4(22)]	C(18) – C(19) – C(20)	122.4(27)	[119.9(28)]
C(5) – C(6) – C(7)	120.9(22)	[126.8(24)]	Br – C(20) – C(19)	122.2(23)	[120.9(24)]
C(5) – C(6) – C(14)	109.9(22)	[107.3(24)]	Br – C(20) – C(21)	117.5(22)	[119.4(24)]
C(7) – C(6) – C(14)	105.6(22)	[102.8(22)]	C(19) – C(20) – C(21)	120.3(29)	[119.6(29)]
C(6) – C(7) – C(8)	117.9(23)	[114.5(20)]	C(20) – C(21) – C(22)	120.8(27)	[121.2(30)]
C(6) – C(7) – C(11)	103.8(22)	[104.9(21)]	C(17) – C(22) – C(21)	115.2(25)	[117.1(27)]
C(8) – C(7) – C(11)	108.3(23)	[104.0(20)]			

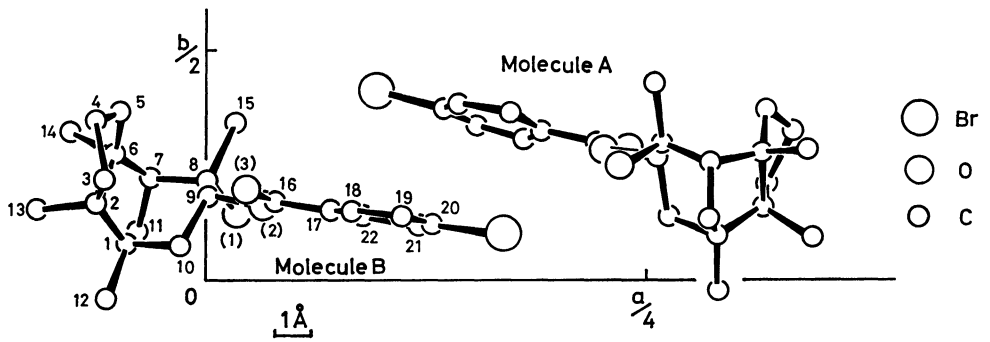


Fig. 1. The atomic arrangement in the crystallographically independent molecules of α-pompene diol mono-*p*-bromobenzoate viewed along the c-axis. (This figure corresponds to the equivalent positions of "1/2−*x*, 1−*y*, 1/2+*z*" relative to the original "*x*, *y*, *z*" coordinates.)

Table 4. Equations of planes and displacements (Å) of the atoms from mean planes
X, *Y*, *Z* are orthogonal co-ordinates (Å), values for molecule B in square brackets.

Plane (1): C(1), C(7), C(8), C(10)
$0.5358X + 0.5312Y + 0.6563Z = 15.5556$
$[0.2632X - 0.6758Y + 0.6885Z = 1.7983]$

C(1)	−0.04 [0.01]	C(10)	0.04 [−0.02]	C(12)	−1.16 [1.04]
C(7)	0.04 [−0.02]	C(9)	0.60 [−0.64]	C(15)	−2.84 [2.91]
C(8)	−0.04 [0.03]	C(11)	−0.88 [0.85]		

Plane (2): C(1), C(2), C(6), C(7)
$-0.5314X + 0.4597Y + 0.7115Z = 4.7264$
$[0.7358X + 0.2635Y - 0.1239Z = 19.1385]$

C(1)	0.01 [0.02]	C(7)	−0.02 [−0.02]	C(15)	2.10 [2.29]
C(2)	−0.02 [−0.03]	C(11)	−0.76 [−0.69]		
C(6)	0.02 [0.03]	C(12)	−0.64 [−0.67]		

Plane (3): C(2), C(3), C(5), C(6)
$0.9971X - 0.0083Y - 0.0763Z = 7.9342$
$[0.9538X - 0.3000Y - 0.0168Z = 21.9081]$

C(2)	0.01 [−0.02]	C(6)	−0.01 [0.02]	C(13)	1.33 [−1.41]
C(3)	−0.01 [0.02]	C(4)	0.65 [−0.65]		
C(5)	0.01 [−0.02]	C(14)	1.23 [−1.22]		

Plane (4): C(16), C(17), C(18), C(19)
$0.2691X + 0.9392Y + 0.2131Z = 12.5214$
$[0.1393X + 0.9893Y + 0.0427Z = 13.2438]$

C(16)	0.01 [−0.02]	C(20)	0.02 [−0.03]	O(3)	0.28 [0.12]
C(17)	−0.01 [0.02]	C(21)	−0.01 [−0.09]	Br	0.11 [−0.04]
C(18)	−0.01 [0.02]	C(22)	−0.03 [−0.07]		
C(19)	0.01 [−0.02]	O(2)	−0.35 [−0.12]		

Plane (5): O(2), C(16), O(3)
$0.2273X + 0.9712Y - 0.0708Z = 10.9562$
$[0.1606X + 0.9766Y + 0.1429Z = 14.1791]$

O(2)	−0.01 [0.01]	C(18)	−0.39 [−0.08]	C(21)	0.27 [0.06]
C(16)	0.01 [−0.02]	C(19)	−0.39 [−0.12]	C(22)	0.28 [0.07]
O(3)	−0.01 [0.01]	C(20)	−0.07 [0.00]	Br	−0.00 [0.00]
C(17)	−0.04 [0.04]				

for the O(2) atom in this cyclohexane ring. The atoms C(1), C(7), C(8), and C(10) of this ring are closely coplanar and atoms C(11) and C(9) are displaced by −0.88 [0.85] and 0.60 [−0.64] Å from the plane.

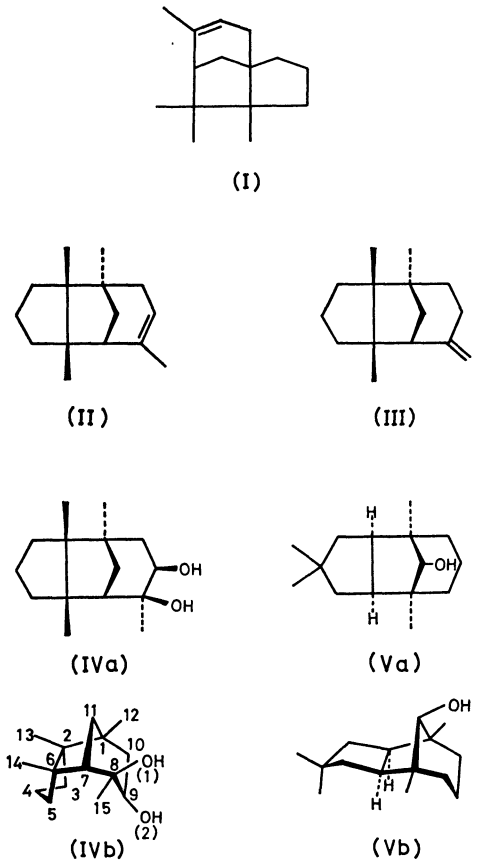
Substituted carbocyclic and heterocyclic bicyclo-[3.2.1]octane moieties are found in a wide variety of natural products. Available X-ray results[10] show that the displacement of the unique bridging atom, C(11), of bicyclo[3.2.1]octane moieties from the plane which is defined by the four carbon atoms (C(1), C(7), C(8), and C(10)) in the cyclohexane ring (−0.88 [0.85] Å in the present α-pompene derivative and 0.80 Å in α-caryophyllene alcohol) exceeds the value of 0.73 Å appropriate to an ideal cyclohexane ring.[11]

The distortion of the cyclohexane ring in α-pompene derivative is also reflected in the valency angles, which are similar to those in α-caryophyllene alcohol.[10] The angle C(1)–C(11)–C(7), 101 [104]°, (α-caryophyllene alcohol 104°) is considerably less than, and the angles C(1)–C(10)–C(9), 115 [111]°, and C(7)–C(8)–C(9), 110 [110]°, (α-caryophyllene alcohol 112 and 112°) are slightly greater than the ideal tetrahedral value. In addition, C(10)–C(1)–C(11), 106 [108], and C(8)–C(7)–C(11), 108 [104]° are also slightly less than the tetrahedral value (α-caryophyllene alcohol 111 and 110°).

The cyclopentane angles in the present α-pompene derivative average 102 [103] in the central ring (C(1), C(2), C(6), C(7), and C(11)) and 104 [103]° in the terminal ring (C(2), C(3), C(4), C(5), and C(6)); these values are consistent with the values which observed in a typical envelope type. Both five-membered rings adopt envelope conformations, in which atoms C(11) and C(4) constitute the flap of the envelopes and have displacements of 0.76 [−0.69] and 0.65 [−0.65] Å, respectively, from the four-atom planes (C(1), C(2), C(6), C(7) and C(2), C(3), C(5), C(6)) of the envelope forms.

The five-membered rings of the bicyclo[3.2.1]octane fragments in α-caryophyllene alcohol derivative[10] and in beyeran-3α-ol derivative[12] exist in envelope conformations. But in a number of other natural product derivatives the conformation of the five-membered ring in the bicyclo[3.2.1]octane fragment is intermediate between the half-chair and envelope forms and closer to the former.[11]

The twin-envelope conformation of the bicyclo[3.3.0]-octane fragment in the present α-pompene derivative has a notable resemblance to the "extended crown" conformation of the eight-membered ring in several cyclooctane derivatives.[13] In contrast to this, the conformation of the bicyclo[3.3.0]octane fragment in



α-caryophyllene alcohol derivative[10] is similar to the "boat-chair" conformation of the eight-membered ring.[13]

The angles C(10)–C(1)–C(2) and C(8)–C(7)–C(6) are both 113 [115] and 118 [115]°, respectively, and the corresponding angles in bicyclo[3.2.1]octane have a mean value of 109°.[11] The bridgehead angles C(1)–C(2)–C(3) and C(7)–C(6)–C(5) of the bicyclo[3.3.0]-octane fragment in the present α-pompene derivative are 119 [112] and 121 [127]° respectively, and are noticeably greater than the ideal tetrahedral value. On the other hand, the mean C(sp^3)–C(sp^3) bond length in the present molecule is 1.56 [1.57] Å, but the C(2)–C(6) length, 1.67 [1.76], and the C(8)–C(15) length, 1.62 [1.69] Å, are appreciably longer than the expected value. These values suggest that the following non-bonded contacts cause greater strain to the α-pompene derivative: C(3)···C(10), 3.01 [3.02], C(3)···C(9), 3.31 [3.21], C(5)···C(15), 3.31 [3.35], C(5)···C(9), 3.17 [3.20], and C(13)···C(14), 2.89 [2.93] Å. The angles C(1)–C(2)–C(13), 111 [113] and C(2)–C(1)–C(12), 116 [112]°, are also significantly greater than the tetrahedral value, because of the repulsion of the two adjacent methyl groups, C(12) and C(13). In order to clarify the presence of such a greater strain, the conformational analysis by Boyd's method[14] of the α-pompene derivative and related compounds is now under investigation.[15]

The bond distances in the *p*-bromobenzoate group are within the expected values: C–C ring system 1.37

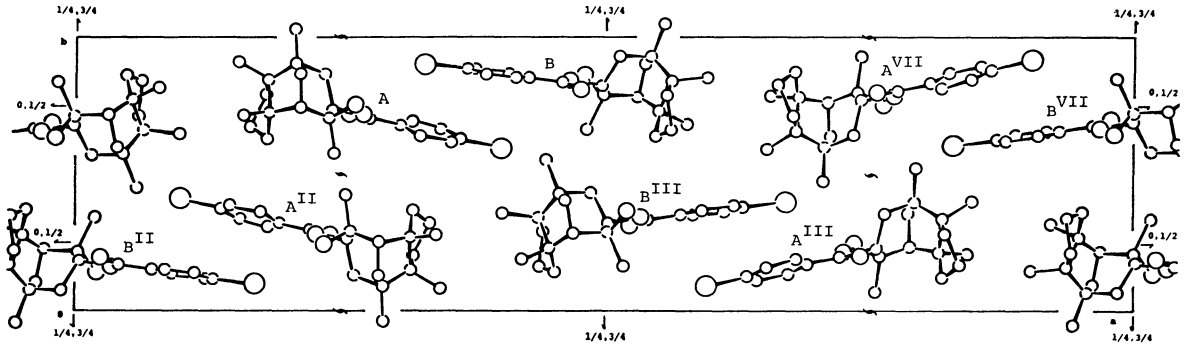


Fig. 2. The molecular arrangement in this crystal viewed along the c-axis.

Table 5. Intermolecular distances (≤3.8 Å)

O(1)A···O(3)A^{I}	2.72	C(15)B···C(11)B^{III}	3.80
O(3)B···O(1)B^{I}	2.77	O(3)B···C(14)B^{IV}	3.61
O(1)A···C(16)A^{I}	3.66	C(5)B···C(17)B^{IV}	3.67
O(1)A···C(18)A^{I}	3.27	C(16)B···C(12)B^{IV}	3.68
O(3)B···C(9)B^{I}	3.64	C(17)B···C(12)B^{IV}	3.70
C(7)A···O(3)A^{I}	3.65	C(13)B···C(14)A^{V}	3.67
C(8)A···O(3)A^{I}	3.57	O(1)A···C(12)A^{VI}	3.61
C(18)B···O(1)B^{I}	3.66	C(12)A···O(3)A^{VI}	3.52
C(15)A···O(3)A^{II}	3.48	C(12)A···C(16)A^{VI}	3.70
C(15)A···C(16)A^{II}	3.53	C(12)A···C(18)A^{VI}	3.72

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I	$x, y, z+1$	II	$1/2-x, 1-y, 1/2+z$
III	$1-x, -1/2+y, 1/2-z$	IV	$1-x, -1/2+y, 3/2-z$
V	$1/2+x, 3/2-y, 2-z$	VI	$1/2-x, 2-y, 1/2+z$
VII	$1/2+x, 3/2-y, 1+z$		

[1.38], C–C single bond 1.53 [1.55], C–O 1.31 [1.29], C=O 1.21 [1.24] and C–Br 1.88 [1.85] Å. These distances are in good agreement with those found in other *p*-bromobenzoate groups.[16] The *p*-bromobenzoate ester moieties are not completely planar; the dihedral angle between the plane of C(16)—C(22) and the plane C(16), C(17), O(2), O(3) is 16.6 [5.9]°. The bromine atom (Br–A) is displaced by a small amount from the C(17)—C(20) plane (0.11 Å). This small displacement from coplanarity is probably due to the effects of the non-bonded interaction: Br–A···C(15)B, 3.83; C(21)A···C(21)B, 3.51; and Br–B···C(22)A, 3.61 Å. The molecular arrangement in this crystal viewed along the c-axis is shown in Fig. 2. Selected intermolecular distances were calculated, and the most significant contacts ($\leq$3.80 Å) are summarized in Table 5. The two molecules in an asymmetric unit form a dimeric unit with van der Waals contacts between the *p*-bromobenzoate moieties. Along the c-axis these dimeric unit are connected by the intermolecular hydrogen bonds, O(1)A···O(3)A^{I}, 2.72 and O(3)B···O(1)B^{I}, 2.77 Å; therefore, a linear chain is present parallel to this direction. Moreover, several short contacts are found, as shown in Table 5. The shortest contact except for the hydrogen bond is O(1)A··· C(18)A^{I}, 3.27 Å.

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2) (−)-*β*-Pompene (III), which contains an *exo* double bond, is an isomer of (+)-α-pompene (II), which contains an endo double bond. Since α-pompene was coincident with the structure which had been proposed a year before for a sesquiterpene hydrocarbon isolated from another liverwort, *Gymnomitrion obtusum* (J. D. Connolly, A. E. Harding, and I. M. S. Thornton, *Chem. Commun.*, **1972**, 1320, the identity of both hydrocarbons was confirmed using the spectra kindly sent by Dr. J. D. Connolly.).

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9) We used the name "*cis*" (IVb) and "*trans*" (Vb) in order to distinguish the two different types of the overall configuration of tricyclo[5.3.1.$0^{2,6}$]undecane framework.

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