# Structure and Absolute Stereochemistry of the Sesquiterpene Alcohol (−)-Myliol: *X*-Ray Analysis of the *p*-Bromobenzoate

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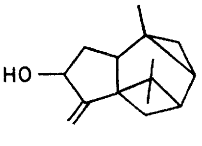
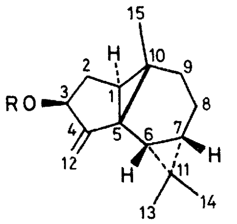
The structure and absolute configuration of the novel sesquiterpene alcohol, (−)-myliol ($C_{15}H_{22}O$) have been determined by *X*-ray analysis of its *p*-bromobenzoate (III). Crystals of the *p*-bromobenzoate (III) are triclinic, space group $P1$, $a = 10.37(1)$, $b = 10.20(1)$, $c = 10.39(1)$ Å, $\alpha = 107.8(1)$, $\beta = 71.6(1)$, $\gamma = 110.3(1)°$, $Z = 2$, with two independent molecules in an asymmetric unit. The structure was solved by the heavy-atom method, and refined by block-diagonal least-squares to $R$ 0.085 over the 1 956 independent observed reflections. The absolute configuration was determined by the anomalous dispersion effect. The two molecules in the asymmetric unit have similar geometries, and each contains a novel fused 5,3,6,3-tetracyclic ring system. The two cyclopropane rings in this fused ring are in conjugation and the central cyclopropane ring conjugates further with an *exo*-double bond. The cyclopentane ring in this skeleton has an envelope conformation and the cyclohexane ring is considerably distorted by the two fused cyclopropane rings.

THE compound (—)-myliol, $C_{15}H_{22}O$, was isolated from a leafy liverwort, *Mylia taylorii* (Hook.) Gray, by V. Benešová and co-workers [1,2] who assigned to it the sesquiterpene structure (I) based on extensive chemical and spectroscopic evidence. However, this structure was unsatisfactory in several respects. In order to establish the structure and absolute stereochemistry of (—)-myliol, a single-crystal *X*-ray diffraction analysis of the *p*-bromobenzoyl derivative (III) was undertaken. A preliminary account of this analysis has been published.[3]



(I)



(II) R = H

(III) R = CO·C$_6$H$_4$Br

## EXPERIMENTAL

Crystals of the *p*-bromobenzoate (III) were obtained as colourless thin plates, m.p. 148—149 °C from hexane–ethyl acetate, elongated along the *c* axis. Preliminary values of cell dimensions were obtained from oscillation and Weissenberg photographs taken with Ni-$K_\alpha$ ($\lambda = 1.659\,1$ Å) radiation, and were subsequently adjusted by a least-squares treatment of the $\theta$, $\chi$, and $\phi$ setting angles of eighteen reflections measured on a Rigaku four-circle automatic diffractometer with graphite-reflected Mo-$K_\alpha$ radiation.

*Crystal Data.*—$C_{22}H_{25}O_2Br$, $M = 401.3$. Triclinic, $a = 10.37(1)$, $b = 10.20(1)$, $c = 10.39(1)$ Å, $\alpha = 107.8(1)$, $\beta = 71.6(1)$, $\gamma = 110.3(1)°$, $U = 952.9$ Å$^3$, $D_m = 1.38$ (by flotation in $ZnCl_2$ solution), $Z = 2$, $D_c = 1.39$ g cm$^{-3}$, $F(000) = 416$. Mo-$K_\alpha$ radiation, $\lambda = 0.710\,7$ Å; $\mu$(Mo-$K_\alpha$) = 22.7 cm$^{-1}$. Space group $P1$ ($P\bar{1}$ is excluded as the compound is optically active).

Three-dimensional intensity data were collected for a crystal of dimensions 0.35 × 0.28 × 0.18 mm by use of the $2\theta$—$\omega$ scan technique. Integrated intensities were measured throughout a hemisphere for $2\theta < 55.0°$ by scanning over a peak at a rate of 4° min$^{-1}$. Background counts were taken for 3 s at each end of the scan range. A scan width of $(1.0 + 0.4 \tan \theta)$ throughout the $2\theta$ range was used. Of 2 770 independent reflections measured, 1 956 having $I > 3\sigma(I)$ were used in the subsequent structure analysis. Three check reflections, remeasured every 70 reflections, did not alter significantly during data collection. Data were corrected for Lorentz and polarisation factors, but not for absorption effects.

*Structure Analysis and Refinement.*—The structure was solved by the heavy-atom method. The positions of the two independent bromine atoms were determined from the three-dimensional Patterson map. The subsequent analysis based on bromine phases was somewhat complicated by the presence of the false inversion centre in the electron-density map. This difficulty was overcome by careful selection of reasonable atom sites by trial and error. After several trial calculations the non-hydrogen atom skeleton of both molecules was revealed ($R$ 0.270). This model was subsequently refined by block-diagonal least-squares calculations. Four cycles of refinement reduced the value of $R$ to 0.169, and, when anisotropic temperature factors were introduced for the two bromine atoms, $R$ was reduced to 0.130 after four cycles. A difference-Fourier map calculated at this stage showed no spurious peaks, and the estimation of the hydrogen-atom positions from this map was difficult. They were therefore included in further structure-factor calculations at calculated positions, assuming C–H 1.08 Å and tetrahedral valence angles. The positions of the hydrogen atoms were fixed and the isotropic thermal factor $B$ 4.5 was used. Further least-squares refinements using anisotropic temperature factors for all the non-hydrogen atoms and introducing anomalous scattering factors for the bromine atoms ($\Delta f'$ −0.3 and $\Delta f''$ 2.6 taken from ref. 4) converged to $R$ 0.085. For all structure-factor calculations the scattering factors from ref. 4 were used. The weighting scheme was $w = 1.0$ if $|F_o| \geqslant 2.5|F_{min.}|$ and $w = 0.5$ if $|F_o| < 2.5|F_{min.}|$ where $|F_{min.}| = 24.0$. A structure-factor calculation for the enantiomer of formula (II) was carried out to determine the absolute configuration, and $R$ 0.106 was obtained. These results show a very significant difference [5] and indicate that formula (II) represents the correct absolute stereochemistry. All the Figures conform to this configuration. All calculations were performed on a HITAC 8700 computer at Hiroshima University Computation Centre by means of the UNICS program with slight modification.[6] Observed and calculated structure factors, anisotropic thermal parameters, and intermolecular distances are listed in Supplementary Publication No. SUP 22433 (13 pp., 1 microfiche).*

## RESULTS AND DISCUSSION

The atom numbering scheme is depicted in formula (II). Final atom positions with their standard deviations and the calculated co-ordinates of the hydrogen atoms are listed in Tables 1 and 2.

The configurations of the two crystallographically independent myliol *p*-bromobenzoate molecules are illustrated in Figure 1. The two independent molecules have not only the same chirality but also similar conformations. The skeleton of each molecules consists of a 5,3,6,3-tetracyclic ring system, and therefore the previously suggested structure (I) for myliol should be revised. The absolute configuration of the myliol molecule is given by stereostructure (II) with an aromadendrene-type skeleton.[7] This sesquiterpene alcohol seems to be the first naturally occurring example containing two conjugated cyclopropane rings.

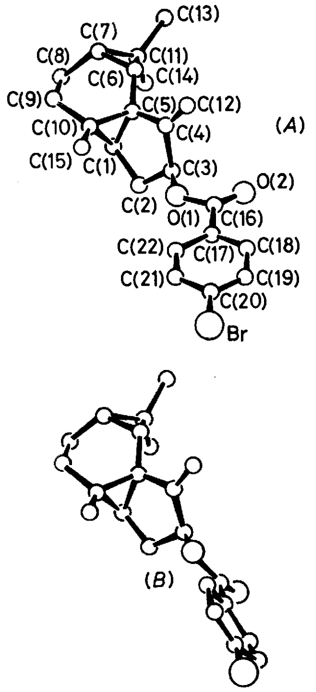


FIGURE 1 Perspective drawings of the two molecules (*A*) and (*B*) of myliol *p*-bromobenzoate, showing the atom numbering

Bond lengths and angles are listed in Table 3, together with their estimated standard deviations, and selected torsion angles are summarized in Table 4. The displacement of atoms from the selected least-squares mean planes are listed in Table 5 with the equations of the planes; values are given for the two molecules of the asymmetric unit, labelled (*A*) and (*B*), those for the

TABLE 1

Fractional co-ordinates (× $10^4$) for non-hydrogen atoms, with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| (*a*) Molecule (*A*) | | | |
| Br | 10 000(3) | 10 000(4) | 0(3) |
| O(1) | 6 435(13) | 7 096(13) | 5 689(14) |
| O(2) | 6 970(17) | 9 452(15) | 6 770(16) |
| C(1) | 4 279(21) | 4 205(21) | 7 319(23) |
| C(2) | 4 350(22) | 5 368(24) | 6 598(27) |
| C(3) | 5 553(19) | 6 593(24) | 6 953(22) |
| C(4) | 6 445(19) | 6 171(21) | 7 635(20) |
| C(5) | 5 590(21) | 4 747(20) | 7 952(23) |
| C(6) | 5 675(21) | 4 512(22) | 9 297(25) |
| C(7) | 4 951(23) | 3 022(21) | 9 613(27) |
| C(8) | 4 136(27) | 1 880(24) | 8 629(27) |
| C(9) | 5 031(27) | 1 965(22) | 7 092(26) |
| C(10) | 5 446(22) | 3 439(22) | 6 756(26) |
| C(11) | 4 400(23) | 4 283(21) | 10 591(23) |
| C(12) | 7 667(19) | 6 928(20) | 7 870(24) |
| C(13) | 4 934(28) | 4 904(24) | 11 971(24) |
| C(14) | 2 943(24) | 4 428(25) | 10 802(28) |
| C(15) | 6 433(23) | 3 550(27) | 5 285(22) |
| C(16) | 6 981(20) | 8 529(21) | 5 788(26) |
| C(17) | 7 712(19) | 8 826(19) | 4 317(21) |
| C(18) | 8 384(23) | 10 285(21) | 4 216(23) |
| C(19) | 9 034(20) | 10 627(21) | 2 890(22) |
| C(20) | 9 001(18) | 9 510(22) | 1 770(20) |
| C(21) | 8 413(21) | 8 078(22) | 1 817(23) |
| C(22) | 7 732(21) | 7 760(21) | 3 129(24) |
| (*b*) Molecule (*B*) | | | |
| Br | −1 382(4) | 3 666(3) | 11 832(4) |
| O(1) | 1 106(14) | 6 266(13) | 5 959(13) |
| O(2) | 108(17) | 3 987(15) | 4 989(15) |
| C(1) | 1 204(18) | 8 545(19) | 3 841(22) |
| C(2) | 379(20) | 7 177(21) | 4 371(23) |
| C(3) | 1 535(22) | 6 666(21) | 4 584(22) |
| C(4) | 2 827(18) | 7 896(20) | 4 599(20) |
| C(5) | 2 762(19) | 9 014(18) | 3 959(22) |
| C(6) | 4 051(21) | 9 695(20) | 2 925(26) |
| C(7) | 4 077(22) | 10 891(20) | 2 347(25) |
| C(8) | 2 670(23) | 11 252(21) | 2 833(27) |
| C(9) | 2 057(22) | 11 334(21) | 4 373(28) |
| C(10) | 1 707(20) | 9 874(22) | 4 800(25) |
| C(11) | 4 307(22) | 9 485(21) | 1 381(21) |
| C(12) | 3 964(22) | 8 052(28) | 5 063(27) |
| C(13) | 5 832(23) | 9 636(25) | 612(25) |
| C(14) | 3 252(24) | 8 478(24) | 578(23) |
| C(15) | 1 190(21) | 10 015(25) | 6 426(24) |
| C(16) | 427(20) | 4 893(20) | 5 955(22) |
| C(17) | 0(20) | 4 580(21) | 7 416(20) |
| C(18) | −837(22) | 3 229(22) | 7 642(25) |
| C(19) | −1 285(27) | 2 928(25) | 8 941(27) |
| C(20) | −852(22) | 3 984(23) | 9 956(23) |
| C(21) | 68(22) | 5 339(21) | 9 789(23) |
| C(22) | 493(20) | 5 687(21) | 8 507(23) |

TABLE 2

Calculated hydrogen atom fractional co-ordinates (× $10^4$), labelled according to their bonded carbon atoms

| | Molecule (*A*) | | | Molecule (*B*) | | |
|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | *x* | *y* | *z* |
| H(1) | 3 142 | 3 795 | 7 609 | 624 | 8 315 | 3 063 |
| H(2a) | 4 523 | 4 969 | 5 486 | −383 | 7 394 | 5 338 |
| H(2b) | 3 380 | 5 683 | 6 980 | −170 | 6 381 | 3 619 |
| H(3) | 5 149 | 7 446 | 7 699 | 1 698 | 5 746 | 3 763 |
| H(6) | 6 716 | 5 261 | 9 182 | 4 608 | 9 519 | 3 548 |
| H(7) | 5 287 | 2 214 | 9 789 | 4 663 | 11 987 | 2 296 |
| H(8a) | 3 121 | 2 053 | 8 786 | 1 932 | 10 437 | 2 268 |
| H(8b) | 3 967 | 838 | 8 807 | 2 826 | 12 273 | 2 615 |
| H(9a) | 4 416 | 1 196 | 6 380 | 1 096 | 11 656 | 4 671 |
| H(9b) | 5 987 | 1 675 | 6 932 | 2 810 | 12 136 | 4 930 |
| H(18) | 8 399 | 11 127 | 5 146 | −1 143 | 2 395 | 6 772 |
| H(19) | 9 530 | 11 721 | 2 781 | −1 951 | 1 890 | 9 120 |
| H(21) | 8 476 | 7 240 | 884 | 441 | 6 107 | 10 663 |
| H(22) | 7 215 | 6 659 | 3 206 | 1 157 | 6 773 | 8 348 |

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

latter being in parentheses; this convention is also followed in the subsequent discussion.

As the presence of two cyclopropane rings in a tetracyclic skeleton imposes some strain on the myliol molecule, the C–C single-bond distances vary over a wide range (1.45—1.58 Å). The C–C bond distances in the two cyclopropane rings in both molecules [mean 1.53 (1.53) Å] are slightly longer than those values found from recent structural studies.[8,9] The present conjugated C(5)–C(6) bond distance between two cyclopropane rings is 1.52 (1.53) Å and this value is the first example for this system. The central cyclopropane ring conjugates further with the C(4)–C(12) *exo*-double bond: C(4)–C(12) and C(4)–C(5), 1.29 (1.35) and 1.49 (1.51) Å. The u.v. absorption band [$\lambda_{max.}$ (EtOH) 217 nm; $\varepsilon$ 4 290] of this alcohol is attributed to the presence of the aforementioned conjugated system. For methyl groups attached to cyclopropane rings, the mean value of the geminal C(Me)–C bond distances at C(11) is 1.52 Å [C(11)–C(13) and C(11)–C(14)] which is shorter than the C(Me)–C distance, 1.57 Å, [C(10)–C(15)]. The bond angles in the cyclopropane rings (mean 60°) are close to their expected value.

The cyclopentane ring in each molecule adopts an

TABLE 3

Bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses

| | Molecule (*A*) | Molecule (*B*) |
|---|---|---|
| (*a*) Distances | | |
| Br–C(20) | 1.92(2) | 1.95(3) |
| O(1)–C(3) | 1.47(3) | 1.50(3) |
| O(1)–C(16) | 1.36(3) | 1.33(3) |
| O(2)–C(16) | 1.16(3) | 1.18(3) |
| C(1)–C(2) | 1.56(4) | 1.53(3) |
| C(1)–C(5) | 1.55(3) | 1.55(3) |
| C(1)–C(10) | 1.53(4) | 1.45(4) |
| C(2)–C(3) | 1.48(4) | 1.56(3) |
| C(3)–C(4) | 1.56(3) | 1.48(3) |
| C(4)–C(5) | 1.49(3) | 1.51(3) |
| C(4)–C(12) | 1.29(3) | 1.35(4) |
| C(5)–C(6) | 1.52(4) | 1.53(4) |
| C(5)–C(10) | 1.52(4) | 1.52(3) |
| C(6)–C(7) | 1.53(4) | 1.51(4) |
| C(6)–C(11) | 1.57(4) | 1.50(4) |
| C(7)–C(8) | 1.50(4) | 1.52(4) |
| C(7)–C(11) | 1.53(4) | 1.53(4) |
| C(8)–C(9) | 1.58(4) | 1.51(4) |
| C(9)–C(10) | 1.53(4) | 1.57(4) |
| C(10)–C(15) | 1.56(4) | 1.58(4) |
| C(11)–C(13) | 1.57(4) | 1.51(4) |
| C(11)–C(14) | 1.51(4) | 1.49(3) |
| C(16)–C(17) | 1.55(4) | 1.54(3) |
| C(17)–C(18) | 1.43(3) | 1.40(3) |
| C(17)–C(22) | 1.37(3) | 1.42(3) |
| C(18)–C(19) | 1.42(3) | 1.38(4) |
| C(19)–C(20) | 1.36(3) | 1.32(4) |
| C(20)–C(21) | 1.38(3) | 1.41(3) |
| C(21)–C(22) | 1.40(4) | 1.38(3) |
| (*b*) Angles | | |
| C(3)–O(1)–C(16) | 118(2) | 116(2) |
| C(2)–C(1)–C(5) | 108(2) | 111(2) |
| C(2)–C(1)–C(10) | 119(2) | 120(2) |
| C(5)–C(1)–C(10) | 59(2) | 61(2) |
| C(1)–C(2)–C(3) | 106(2) | 104(2) |
| O(1)–C(3)–C(2) | 109(2) | 112(2) |
| O(1)–C(3)–C(4) | 111(2) | 107(2) |
| C(2)–C(3)–C(4) | 111(2) | 108(2) |
| C(3)–C(4)–C(5) | 106(2) | 111(2) |
| C(3)–C(4)–C(12) | 126(2) | 128(2) |
| C(5)–C(4)–C(12) | 128(2) | 122(2) |
| C(1)–C(5)–C(4) | 109(2) | 104(2) |
| C(1)–C(5)–C(6) | 127(2) | 126(2) |
| C(1)–C(5)–C(10) | 60(2) | 56(2) |
| C(4)–C(5)–C(6) | 115(2) | 120(2) |
| C(4)–C(5)–C(10) | 119(2) | 117(2) |
| C(6)–C(5)–C(10) | 116(2) | 118(2) |
| C(5)–C(6)–C(7) | 118(2) | 122(2) |
| C(5)–C(6)–C(11) | 125(2) | 130(2) |
| C(7)–C(6)–C(11) | 59(2) | 61(2) |
| C(6)–C(7)–C(8) | 119(2) | 113(2) |
| C(6)–C(7)–C(11) | 62(2) | 59(2) |
| C(8)–C(7)–C(11) | 122(2) | 124(2) |
| C(7)–C(8)–C(9) | 108(2) | 112(2) |
| C(8)–C(9)–C(10) | 115(2) | 113(2) |
| C(1)–C(10)–C(5) | 61(2) | 63(2) |
| C(1)–C(10)–C(9) | 115(2) | 119(2) |
| C(1)–C(10)–C(15) | 119(2) | 121(2) |
| C(5)–C(10)–C(9) | 118(2) | 113(2) |
| C(5)–C(10)–C(15) | 119(2) | 119(2) |
| C(9)–C(10)–C(15) | 115(2) | 113(2) |
| C(6)–C(11)–C(7) | 59(2) | 60(2) |
| C(6)–C(11)–C(13) | 110(2) | 114(2) |
| C(6)–C(11)–C(14) | 127(2) | 123(2) |
| C(7)–C(11)–C(13) | 114(2) | 112(2) |
| C(7)–C(11)–C(14) | 125(2) | 122(2) |
| C(13)–C(11)–C(14) | 112(2) | 115(2) |
| O(1)–C(16)–O(2) | 129(2) | 127(2) |
| O(1)–C(16)–C(17) | 109(2) | 112(2) |
| O(2)–C(16)–C(17) | 121(2) | 121(2) |
| C(16)–C(17)–C(18) | 118(2) | 120(2) |
| C(16)–C(17)–C(22) | 123(2) | 118(2) |
| C(18)–C(17)–C(22) | 120(2) | 121(2) |
| C(17)–C(18)–C(19) | 120(2) | 121(2) |
| C(18)–C(19)–C(20) | 117(2) | 116(3) |
| Br–C(20)–C(19) | 116(2) | 120(2) |
| Br–C(20)–C(21) | 119(2) | 115(2) |
| C(19)–C(20)–C(21) | 126(2) | 125(2) |
| C(20)–C(21)–C(22) | 117(2) | 120(2) |
| C(17)–C(22)–C(21) | 121(2) | 115(2) |

TABLE 4

Selected torsion angles (°)

| | Molecule (*A*) | Molecule (*B*) |
|---|---|---|
| (*a*) Bicyclo[3.1.0]-system | | |
| C(5)–C(1)–C(2)–C(3) | −6.4 | −9.3 |
| C(10)–C(1)–C(2)–C(3) | −70.2 | −76.9 |
| C(1)–C(2)–C(3)–C(4) | 10.9 | 16.5 |
| C(2)–C(3)–C(4)–C(5) | −11.3 | −18.3 |
| C(3)–C(4)–C(5)–C(1) | 6.8 | 11.9 |
| C(3)–C(4)–C(5)–C(10) | 71.9 | 71.0 |
| C(4)–C(5)–C(1)–C(2) | −0.5 | −1.0 |
| C(4)–C(5)–C(1)–C(10) | 67.0 | 67.2 |
| C(10)–C(5)–C(1)–C(2) | −66.6 | −66.2 |
| C(4)–C(5)–C(10)–C(1) | −84.0 | −90.6 |
| C(5)–C(10)–C(1)–C(2) | 94.2 | 81.7 |
| (*b*) Other | | |
| C(10)–C(1)–C(5)–C(6) | −78.5 | −77.5 |
| C(1)–C(5)–C(6)–C(7) | 42.6 | 45.5 |
| C(1)–C(5)–C(6)–C(11) | −28.0 | −31.8 |
| C(10)–C(5)–C(6)–C(7) | −28.2 | −21.6 |
| C(10)–C(5)–C(6)–C(11) | −81.2 | −98.9 |
| C(5)–C(6)–C(7)–C(8) | −2.8 | −3.7 |
| C(5)–C(6)–C(7)–C(11) | −64.0 | −58.8 |
| C(11)–C(6)–C(7)–C(8) | 66.8 | 62.6 |
| C(5)–C(6)–C(11)–C(7) | 75.4 | 70.7 |
| C(6)–C(7)–C(8)–C(9) | 42.7 | 44.8 |
| C(11)–C(7)–C(8)–C(9) | 64.2 | 67.8 |
| C(7)–C(8)–C(9)–C(10) | −55.0 | −62.6 |
| C(8)–C(9)–C(10)–C(1) | −42.0 | −34.8 |
| C(8)–C(9)–C(10)–C(5) | 27.0 | 35.8 |
| C(9)–C(10)–C(1)–C(5) | 70.9 | 76.9 |
| C(9)–C(10)–C(5)–C(6) | 15.0 | 4.8 |
| C(6)–C(11)–C(7)–C(8) | −71.8 | −82.0 |

TABLE 5

Equations of selected mean planes and in square brackets displacements (Å) of atoms from the mean planes; values for molecule (*B*) are in parentheses and follow those for molecule (*A*)

Plane (*a*): C(3)—(5), C(12)

$$-0.3478x + 0.2581y + 0.9013z = 5.2789$$
$$(-0.3371x + 0.2621y + 0.9042z = 5.1512)$$

[C(3) −0.001 (0.003), C(4) 0.002 (−0.011), C(5) −0.001 (0.003), C(12) −0.001 (0.004)]

Plane (*b*): C(1), C(2), C(4), C(5)

$$-0.4481x + 0.2663y + 0.8534z = 4.2578$$
$$(-0.1793x + 0.3595y + 0.9158z = 6.1080)$$

[C(1) 0.003 (−0.005), C(2) −0.002 (0.004), C(3) −0.167 (0.269), C(4) 0.002 (−0.003), C(5) −0.003 (0.005), C(10) 1.208 (−1.167)]

Plane (*c*): C(6), C(7), C(9), C(10)

$$0.9784x - 0.0172y - 0.2059z = 5.2263$$
$$(0.6432x + 0.4390y + 0.6273z = 6.5936)$$

[C(5) 0.262 (0.168), C(6) −0.082 (−0.079), C(7) 0.072 (0.090), C(8) 0.611 (0.609), C(9) −0.071 (−0.107), C(10) 0.085 (0.101)]

Plane (*d*): O(1), O(2), C(16), C(17)

$$0.9937x - 0.0789y + 0.0798z = 5.9940$$
$$(-0.9649x + 0.1769y + 0.1940z = 1.0778)$$

[O(1) −0.002 (−0.005), O(2) −0.002 (−0.005), C(16) 0.005 (0.015), C(17) −0.002 (−0.005)]

Plane (*e*): C(17)—(20)

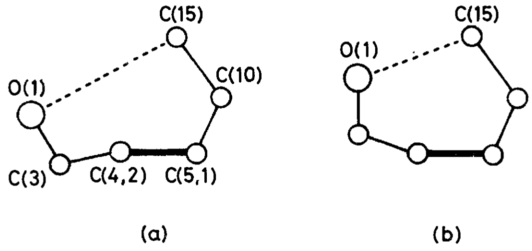
$$0.9941x + 0.0935y + 0.0555z = 5.7905$$
$$(-0.9488x + 0.2593y + 0.1802z = 1.2216)$$

[C(17) 0.003 (−0.003), C(18) −0.006 (0.006), C(19) 0.006 (−0.006), C(20) −0.003 (0.003), C(21) −0.048 (0.084), C(22) −0.012 (0.048), Br −0.107 (0.033)]

envelope conformation, and the oxygen substituent is equatorial; atoms C(1), C(2), C(4), and C(5) are virtually coplanar and atoms C(3) and C(10) are displaced by −0.167 (0.269) and 1.208 (−1.167) Å from the plane. The atom C(3) thus forms the flap of the envelope. Since C(3) and C(10) lie on the opposite side of this ring the bicyclohexane systems has an overall chair-like conformation. The out-of-plane displacement of C(3) is rather small compared with the values determined for other bicyclo[3.1.0]-derivatives[10] and the present cyclopentane ring is considerably flatter, while C(10) is more puckered than in a usual cyclohexane ring.[11] The dihedral angle between the C(1), C(2), C(4), C(5) plane and the C(1), C(5), C(10) cyclopropane ring is 113.3 (113.3)°, and between the C(1), C(2), C(4), C(5), and C(2)—(4) planes is 168.8 (162.6)°. The former value is in good agreement with those for similar compounds involving the cyclopropane ring.[10,12]

The bicyclo[3.1.0]hexane systems in lindenenol[10] and in 3,3-dimethyl-6,6-diphenyl-3-azabicyclo[3.1.0]hexane[13] are also in the chair conformation. However, in a wide variety of natural products containing this system, many studies indicate that the boat is preferred to the chair conformation, though this depends on the nature of the substituents.[14,15] In myliol, the preference for the chair conformation is probably due to intramolecular steric effects, a boat-like conformation being precluded by the non-bonded interaction of C(15) with O(1), as shown in Figure 2. In both molecules the mean C–C bond distance in the cyclopentane ring is 1.53 Å and the *exo*-methylene group C(3)—(5), C(12) is quite planar. The bond angles C(1)–C(10)–C(15) and C(5)–C(10)–C(15) in both molecules are enlarged to 119 (121) and 119 (119)°. These values suggest that the following non-bonded interactions cause greater strain to the cyclopentane rings: C(4) ⋯ C(15) 3.02 (3.03), and C(2) ⋯ C(15) 3.06 (3.05) Å.

The mean bond distance within the cyclohexane ring is 1.53 Å in both molecules, which does not differ significantly from accepted values. However, the cyclohexane ring in both molecules is distorted considerably by its fusion with two cyclopropane rings. The torsion angles for both molecules are summarized in Table 4. The angles for molecule (*B*) are $\omega_{5,6}$ −21.6, $\omega_{6,7}$ −3.7, $\omega_{7,8}$ 44.8, $\omega_{8,9}$ −62.6, $\omega_{9,10}$ 35.8, and $\omega_{10,5}$ 4.8°. These values demonstrate that the cyclohexane ring has a conformation intermediate between a boat and a sofa-form, in which the typical values derived by Bucourt and Hainaut are $\omega_{5,6}$ −22, $\omega_{6,7}$ 0, $\omega_{7,8}$ 40, $\omega_{8,9}$ −60, $\omega_{9,10}$ 40, and $\omega_{10,5}$ 0°.[16,*] This form is classified by them as being in a 1,3-diplanar conformation. In molecule (*A*), the conformation of the cyclohexane ring is closer to that of a deformed boat. This is indicated both by the torsion angles ($\omega_{5,6}$ −28.2, $\omega_{6,7}$ −2.8, $\omega_{7,8}$ 42.7, $\omega_{8,9}$ −55.0, $\omega_{9,10}$ 27.0, $\omega_{10,5}$ 15.0°) and by the near-coplanarity of C(6), C(7), C(9), C(10); atoms C(5) and C(8) of molecule (*A*) are displaced by 0.26 and 0.61 Å respectively from this plane.



(a) (b)

FIGURE 2 A comparison between (a) the chair conformation (this structure) and (b) the corresponding boat conformation (postulated structure) in the bicyclo[3.1.0]-system viewed along the plane defined by atoms C(1), C(2), C(4), and C(5)

The mean bond angle of the cyclohexane rings in both molecules is 116°. The ring angles at positions C(5), C(6), C(7), and C(10) are enlarged to a mean value of 118 (117)° owing to the strain caused by fusion with the two cyclopropane rings. In order to clarify the existence of such great strain a conformational analysis by Boyd's method is now under investigation.[17]

In the *p*-bromobenzoate group, the C(Ph)–Br distance of 1.92 (1.95) Å is slightly larger than reported values (1.85 Å),[8] but values exceeding 1.90 Å have frequently been found.[18] The mean aromatic C–C bond distance is 1.39 (1.38) Å, and the mean intra-annular angle is 120 (120)°. The C($sp^2$)–O [C(16)–O(1) 1.36 (1.33)] and C($sp^3$)–O [C(3)–O(1) 1.47 (1.50) Å] are normal, but the C=O bond distance [C(16)–O(2) 1.16 (1.18)] and

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[*] All the signs of the torsion angles from ref. 6 were changed for comparison with our data.

C(Ph)–C($sp^2$) [C(17)–C(16) 1.55 (1.54) Å] are shorter and longer than expected values. The *p*-bromobenzoate ester is not completely planar; the bromine atom in molecule (*A*) and C(21) in molecule (*B*) are displaced by small amounts from the C(17)—(22) plane (0.11 and 0.08 Å respectively). This small distortion from coplanarity is probably due to the intermolecular interactions: 3.53 Å between Br of molecule (*A*) and C(15) of molecule (*B*) at $x + 1, y, z + 1$, and 3.55 Å between C(21) of molecule (*B*) and C(21) of molecule (*A*) at $x - 1, y, z$.

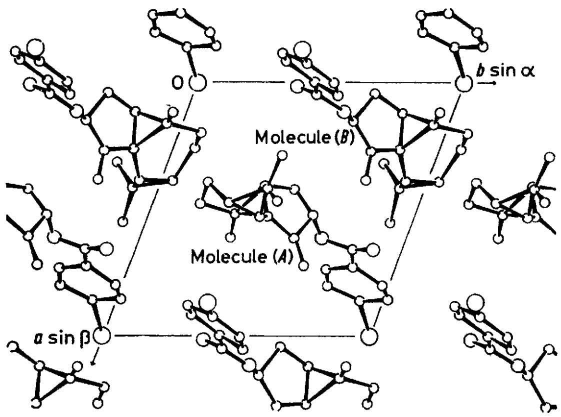

FIGURE 3 The molecular packing in this crystal viewed along the *c* axis

The intramolecular non-bonded contact between the O(2) and C(3) atoms is 2.83 (2.70) Å, and this mode of contact in which O(2) approaches C(3) on the hydrogen side is usually observed in many secondary esters.[19] On the other hand, the unequal non-bonded contacts between O(2) · · · C(4) 3.55 (4.06) and O(2) · · · C(2) 4.01 (3.41) Å in both molecules show that the ester plane is tilted toward C(4) in molecule (*A*) [*ca.* 24° between the planes (*b*) and (*d*) in Table 5] and toward C(2) in molecule (*B*) (*ca.* 24°), respectively (see Figure 1).

The molecular packing in this crystal viewed along the *c* axis is shown in Figure 3. There is no hydrogen bonding in the crystal, the shortest contact being 3.29 Å between C(16) of molecule (*A*) and C(12) of molecule (*B*). Other intermolecular contacts are greater than the sum of the relevant van der Waals radii.

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