The Structure and Absolute Configuration of (—)-2β,9α-Dihydroxyverrucosane isolated from the Liverwort *Mylia verrucosa*: *X*-Ray Analysis of the Mono-*p*-bromobenzoate

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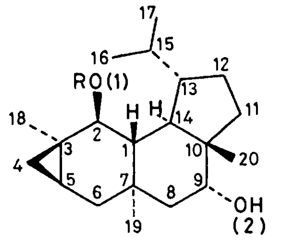
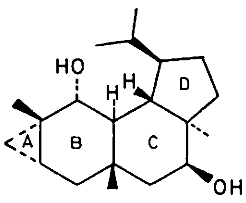
The structure of dihydroxyverrucosane (I), a novel diterpene-diol isolated from the liverwort *Mylia verrucosa* has been determined from single-crystal *X*-ray analysis of the mono-*p*-bromobenzoate (II) by the heavy-atom method. The crystals were monoclinic, $a = 6.670(1)$, $b = 19.269(1)$, $c = 10.379(1)$ Å, $\beta = 112.6(4)°$, space group $P2_1$, $Z = 2$. Block-diagonal least-squares refinement based on 1 929 independent reflections converged to R 0.078. The absolute configuration was established by the anomalous dispersion effect. The molecule contains a 3,6,6,5-tetracyclic ring system in which ring A is considerably distorted by fusion with the cyclopropane ring A. Ring C adopts a chair conformation and ring D is a conformation somewhere between a half-chair and β-envelope.

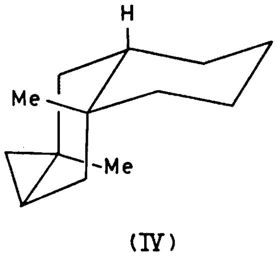
(—)-2β,9α-DIHYDROXYVERRUCOSANE, $C_{20}H_{34}O_2$, is a diterpene-diol with a novel carbon skeleton, named verrucosane, which has been isolated from the liverwort *Mylia verrucosa* Lindb. together with other diterpenoids with the same carbon skeleton. Structure (I) for the diol was elucidated on the basis of extensive chemical reactions and spectral evidence.[1] *X*-Ray analysis of the mono-*p*-bromobenzoate was undertaken in order to confirm the structural assignment and to obtain more detailed information of the molecular conformation.



(I) R = H
(II) R = COC$_6$H$_4$Br



(III)



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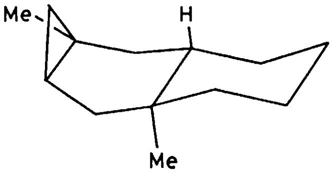

(V)

EXPERIMENTAL

The mono-*p*-bromobenzoate (II), m.p. 205—206 °C, was recrystallized from hexane–ethyl acetate (4 : 1) as monoclinic colourless prisms. The space group and the initial unit-cell parameters were obtained from oscillation and Weissenberg photographs taken with Ni-K_α radiation (λ 1.659 1 Å). Accurate-unit cell parameters were obtained by a least-squares treatment of $(\theta,\phi,\chi)_{hkl}$ values of 18 reflections measured on a Rigaku automatic single-crystal diffractometer with graphite-reflected Mo-K_α radiation.

Crystal Data.—$C_{27}H_{37}BrO_3$, $M = 489.5$. Monoclinic, $a = 6.670(1)$, $b = 19.269(1)$, $c = 10.379(1)$ Å, $\beta = 112.6(4)°$, $U = 1\,231.3$ Å^3, $D_m = 1.31$ g cm^{-3} (by flotation in $ZnCl_2$ solution), $Z = 2$, $D_c = 1.31$ g cm^{-3}, $F(000) = 516$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 17.8 cm^{-1}. Space group $P2_1$ (from systematic absences and optical activity).

Three-dimensional intensity data were collected using the 2θ—ω scan technique. The integrated intensities were measured for $2\theta < 55.0°$ by scanning over a peak at a rate of 4° min^{-1}. The background counts were taken for 3 s at each end of the scan range. A scan width of $(1.0 + 0.4\text{-}\tan\theta)$ throughout the 2θ range was used. Instrument and crystal stability were monitored throughout a course of data collection by re-measuring periodically the intensities for three standard reflections and these showed no significant variation. 1 929 Independent reflections satisfied the criterion $I > 3\sigma(I)$, and were corrected for Lorentz and polarization effects and used in the structure analysis. No allowance was made for absorption (0.40 × 0.30 × 0.20 mm).

Structure Analysis and Refinement.—The bromine coordinate was determined from the inspection of the three-dimensional Patterson synthesis and the analysis proceeded on the basis of the phase determined by the bromine atom. The analysis was somewhat complicated initially by the inevitable presence of the pseudo-mirror symmetry in the first (heavy-atom phased) electron-density distribution. This was overcome by careful selection of atomic sites from this map, and the structure was completely revealed after several trial calculations. They were refined by use of block-diagonal least-squares calculations. The bromine atom was refined anisotropically and both the oxygen and carbon atoms isotropically. The R-factor was reduced from 0.228 to 0.112. Refinement was continued by allowing an anisotropic temperature factor for all 31 non-hydrogen atoms and several cycles reduced R to 0.097. The difference 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). These atomic positions were fixed and the isotropic thermal factor $B = 4.5$ was used. Further refinement converged at R 0.093.

To establish the absolute configuration the anomalous scattering corrections for the bromine atom were introduced into the structure-factor calculations (values for $\Delta f'$ and $\Delta f''$ were taken from ref. 2). For co-ordinates corresponding to the absolute stereochemistry represented by (III), R was 0.095, whereas for its enantiomer (I) it was 0.091. The highly significant difference[3] indicated that the enantiomer (I) correctly represented the absolute stereochemistry. Further least-squares iterations based on the parameters for the structure (I) with the anomalous dispersion effect reduced R to 0.079. In the structure-factor calculations scattering factors were taken from ref. 2. The weighting scheme used in the least-squares calculations was of the form $w = 1.0$ if $|F_o| \geqslant 2.5|F_{\text{min.}}|$ and $w = 0.5$ if $|F_o| < 2.5|F_{\text{min.}}|$ where $|F_{\text{min.}}| = 2.5$. All the figures are in agreement with configuration (I). All calculations were performed on HITAC 8700 computer at the Hiroshima University Computation Center by means of the UNICS program with slight modifications.[4] The observed and calculated structure factors, $10|F_o|$ and $10|F_c|$, and anisotropic thermal parameters have been listed in Supplementary Publication No. SUP 22722 (6 pp.).*

RESULTS AND DISCUSSION

The atom labelling system used in analysis for the non-hydrogen skeleton is shown in formula (I) and a projected sketch of the molecule is given in Figure 1. Table 1 lists the final fractional co-ordinates for the non-hydrogen atoms, and Table 2 the calculated co-ordinates of the hydrogen atoms. The present X-ray analysis has established the structure of 2,9-dihydroxyverrucosane to be in accord with that obtained from chemical and spectroscopic evidence. Consequently, the absolute configuration of the diol is given by the stereostructure (I) consisting of a novel fused 3,6,6,5-tetracyclic ring system of the *cis-trans-anti-trans*-type.

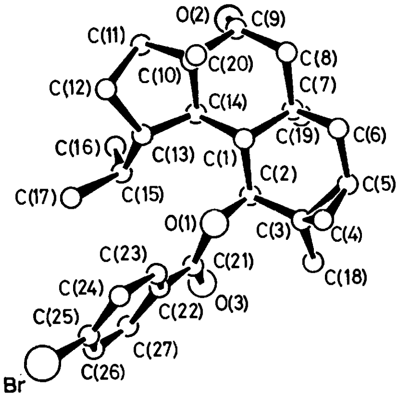

FIGURE 1 Perspective drawing of the mono-*p*-bromobenzoate showing the atom numbering

TABLE 1

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

Atom	*x*	*y*	*z*
Br	−1 198(3)	2 500(2)	−403(8)
O(1)	6 747(13)	4 334(4)	4 468(9)
O(2)	10 578(16)	7 096(5)	5 042(12)
O(3)	8 839(14)	3 537(5)	4 043(10)
C(1)	7 970(20)	5 466(6)	5 373(12)
C(2)	8 661(21)	4 700(6)	5 477(13)
C(3)	9 298(24)	4 358(7)	6 879(14)
C(4)	7 539(32)	4 333(9)	7 458(18)
C(5)	9 490(31)	4 810(8)	8 156(15)
C(6)	9 129(31)	5 573(9)	7 955(17)
C(7)	9 484(23)	5 872(7)	6 700(13)
C(8)	8 891(26)	6 636(7)	6 605(17)
C(9)	8 515(23)	7 000(7)	5 217(15)
C(10)	7 012(22)	6 602(6)	4 032(14)
C(11)	6 822(25)	6 834(7)	2 594(17)
C(12)	5 676(26)	6 207(8)	1 580(15)
C(13)	6 536(21)	5 568(6)	2 544(13)
C(14)	7 840(19)	5 855(6)	4 035(12)
C(15)	7 791(23)	5 076(7)	1 961(13)
C(16)	9 792(27)	5 421(9)	1 796(18)
C(17)	6 263(27)	4 742(8)	577(14)
C(18)	10 906(29)	3 765(8)	7 181(16)
C(19)	11 941(22)	5 782(8)	6 905(15)
C(20)	4 734(23)	6 622(8)	4 129(20)
C(21)	7 046(20)	3 782(6)	3 852(13)
C(22)	5 026(21)	3 459(6)	2 873(12)
C(23)	3 003(22)	3 689(8)	2 779(16)
C(24)	1 133(26)	3 387(8)	1 786(17)
C(25)	1 255(22)	2 893(7)	898(14)
C(26)	3 344(26)	2 665(7)	998(16)
C(27)	5 171(24)	2 953(7)	1 967(15)

TABLE 2

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

	x	*y*	*z*
H(1)	6 344	5 455	5 312
H(2)	10 156	4 668	5 285
H(4a)	7 396	3 901	8 018
H(4b)	5 972	4 564	6 869
H(5)	10 682	4 928	9 185
H(6a)	10 256	5 811	8 901
H(6b)	7 506	5 666	7 852
H(8a)	10 218	6 914	7 414
H(8b)	7 453	6 692	6 813
H(9)	7 804	7 519	5 240
H(11a)	8 391	6 975	2 581
H(11b)	5 819	7 326	2 288
H(12a)	6 145	6 200	730
H(12b)	3 943	6 254	1 259
H(13)	5 230	5 280	2 591
H(14)	9 496	5 807	4 142
H(15)	8 395	4 664	2 698
H(23)	2 882	4 128	3 439
H(24)	−457	3 535	1 732
H(26)	3 547	2 243	413
H(27)	6 717	2 801	1 963

The bond lengths and bond angles are listed in Table 3 together with their standard deviations. Most bond lengths and angles for the molecule are not significantly different from the expected values.[5] Severe distortions, however, are observed in the bond angles of ring B due to the presence of the cylopropane ring. The displacement of atoms from the selected least-squares mean planes are listed in Table 4 with the equations of the planes. The torsion angles within each ring are given in Table 5.

The cyclopropane ring A has a β-configuration and a mean C–C bond distance (1.53 Å) slightly larger than those values found in recent structure determinations.[6,7] The bond angles in the cyclopropane ring are close to their expected values (*ca.* 60°).

The fusion of the cyclopropane ring causes the dis-

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* For details of Supplementary Publications see Notice to Authors No. 7, in *J.C.S. Perkin II*, 1979, Index issue.

TABLE 3

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

(a) Distances

Br–C(25)	1.84(2)	C(9)–C(10)	1.47(2)
O(2)–C(2)	1.48(2)	C(10)–C(11)	1.52(2)
O(1)–C(21)	1.30(2)	C(10)–C(14)	1.54(2)
O(2)–C(9)	1.47(2)	C(10)–C(20)	1.56(3)
O(3)–C(21)	1.23(2)	C(11)–C(12)	1.59(3)
C(1)–C(2)	1.54(2)	C(12)–C(13)	1.55(2)
C(1)–C(7)	1.57(2)	C(13)–C(14)	1.56(2)
C(1)–C(14)	1.55(2)	C(13)–C(15)	1.53(2)
C(2)–C(3)	1.50(2)	C(15)–C(16)	1.56(2)
C(3)–C(4)	1.51(3)	C(15)–C(17)	1.55(2)
C(3)–C(5)	1.55(3)	C(21)–C(22)	1.48(2)
C(3)–C(18)	1.52(3)	C(22)–C(23)	1.39(2)
C(4)–C(5)	1.53(3)	C(22)–C(27)	1.38(2)
C(5)–C(6)	1.49(3)	C(23)–C(24)	1.40(2)
C(6)–C(7)	1.52(3)	C(24)–C(25)	1.35(2)
C(7)–C(8)	1.52(2)	C(25)–C(26)	1.43(2)
C(7)–C(19)	1.58(2)	C(26)–C(27)	1.37(2)
C(8)–C(9)	1.53(2)		

(b) Angles

C(2)–O(1)–C(21)	119(1)	C(9)–C(10)–C(14)	111(1)
C(2)–C(1)–C(7)	110(1)	C(9)–C(10)–C(20)	108(1)
C(2)–C(1)–C(14)	116(1)	C(11)–C(10)–C(14)	100(1)
C(7)–C(1)–C(14)	110(1)	C(11)–C(10)–C(20)	110(1)
O(1)–C(2)–C(1)	105(1)	C(14)–C(10)–C(20)	112(1)
O(1)–C(2)–C(3)	109(1)	C(10)–C(11)–C(12)	105(1)
C(1)–C(2)–C(3)	117(1)	C(11)–C(12)–C(13)	102(1)
C(2)–C(3)–C(4)	115(1)	C(12)–C(13)–C(14)	107(1)
C(2)–C(3)–C(5)	119(1)	C(12)–C(13)–C(15)	111(1)
C(2)–C(3)–C(18)	117(1)	C(14)–C(13)–C(15)	116(1)
C(4)–C(3)–C(5)	60(1)	C(1)–C(14)–C(10)	111(1)
C(4)–C(3)–C(18)	119(2)	C(1)–C(14)–C(13)	122(1)
C(5)–C(3)–C(18)	115(1)	C(10)–C(14)–C(13)	105(1)
C(3)–C(4)–C(5)	61(1)	C(13)–C(15)–C(16)	114(1)
C(3)–C(5)–C(4)	59(1)	C(13)–C(15)–C(17)	111(1)
C(3)–C(5)–C(6)	119(2)	C(16)–C(15)–C(17)	111(1)
C(4)–C(5)–C(6)	118(2)	O(1)–C(21)–O(3)	124(1)
C(5)–C(6)–C(7)	115(2)	O(1)–C(21)–C(22)	114(1)
C(1)–C(7)–C(6)	108(1)	O(3)–C(21)–C(22)	122(1)
C(1)–C(7)–C(8)	111(1)	C(21)–C(22)–C(23)	121(1)
C(1)–C(7)–C(19)	110(1)	C(21)–C(22)–C(27)	119(1)
C(6)–C(7)–C(8)	107(1)	C(23)–C(22)–C(27)	120(1)
C(6)–C(7)–C(19)	110(1)	C(22)–C(23)–C(24)	119(1)
C(8)–C(7)–C(19)	110(1)	C(23)–C(24)–C(25)	122(2)
C(7)–C(8)–C(9)	117(1)	Br–C(25)–C(24)	122(1)
O(2)–C(9)–C(8)	111(1)	Br–C(25)–C(26)	120(1)
O(2)–C(9)–C(10)	109(1)	C(24)–C(25)–C(26)	119(1)
C(8)–C(9)–C(10)	111(1)	C(25)–C(26)–C(27)	120(2)
C(9)–C(10)–C(11)	116(1)	C(22)–C(27)–C(26)	121(2)

tortion of the conformation of ring B. It can be described as the flattened skew conformation observed in a typical cyclohexane ring, with the torsion angles around C(2)–C(3) and C(3)–C(5) constrained to be close to 0° (7.2 and 2.7°).[8] Thus, as shown in Table 4, the atoms C(2), C(3), C(5), and C(6) are closely planar and the atoms C(1) and C(7) are displaced unequally on opposite sides of this plane (0.21 and –0.59 Å). The ring angles C(1)–C(2)–C(3), C(2)–C(3)–C(5), C(3)–C(5)–C(6), and C(5)–C(6)–C(7) have an enlarged mean of 117°, but the angles C(2)–C(1)–C(7) and C(1)–C(7)–C(6) are 110 and 108°. These values are very similar to those of 9-*p*-bromobenzoyloxy-1,4,4,8-tetramethyltricyclo[$5.4.0.0^{3,5}$]undecane.[7] The bond distance C(3)–C(18), 1.52 Å, is normal, but the angle C(2)–C(3)–C(18), 117°, is noticeably large, because of the distortion in ring B and the non-bonded repulsion, O(3) · · · C(18), 3.04 Å.

The cyclohexane ring B is *trans*-fused to the central cyclohexane ring C, so that the tricyclo[$5.4.0.0^{3,5}$]-undecane system in this molecule has a *trans*-decalin-like skeleton (V). A number of investigations of the conformation of the tricyclo[$5.4.0.0^{3,5}$]undecane ring system have been carried out,[9,10] and it was concluded that the ring system may be regarded as having a conformation like that of *trans*-decalin. Recently, on the basis of c.d., n.m.r. spectroscopic, and *X*-ray crystallographic investigations, it was found that this system could consist of *cis*-decalin-type derivatives (IV) depending on

TABLE 4

Equations of selected mean planes and displacements (Å) of the atoms from the mean planes

Plane (a): C(2), C(3), C(5), C(6)

$$-0.9733x - 0.1449y - 0.1783z = 0.0351$$

C(1) 0.215, C(2) 0.002, C(3) –0.011, C(4) 1.265, C(5) 0.017, C(6) –0.005, C(7) –0.592

Plane (b): C(1), C(7), C(9), C(10)

$$-0.9426x + 0.1503y + 0.2983z = 1.6314$$

C(1) –0.021, C(7) 0.023, C(8) 0.554, C(9) –0.023, C(10) 0.022, C(14) –0.713

Plane (c): C(12), C(13), C(14)

$$-0.9816x - 0.0073y + 0.1910z = 2.0277$$

C(10) 0.529, C(11) –0.176, C(12) 0.000, C(13) 0.000, C(14) 0.000

Plane (d): O(1), O(3), C(21), C(22)

$$-0.3617x - 0.5620y + 0.7439z = 3.2391$$

O(1) –0.001, O(3) –0.001, C(21) 0.002, C(22) –0.001

Plane (e): C(22), C(23), C(24), C(25)

$$-0.2736x - 0.7015y + 0.6581z = 2.2852$$

C(22) 0.004, C(23) –0.007, C(24) 0.007, C(25) –0.004, C(26) –0.002, C(27) –0.008, Br 0.013

TABLE 5

Selected torsion angles (°)

C(7)–C(1)–C(2)–C(3)	40.7
C(14)–C(1)–C(2)–C(3)	13.7
C(2)–C(1)–C(7)–C(8)	–178.0
C(14)–C(1)–C(7)–C(8)	49.0
C(2)–C(1)–C(14)–C(10)	176.0
C(2)–C(1)–C(14)–C(13)	51.8
C(7)–C(1)–C(14)–C(13)	–177.5
C(1)–C(2)–C(3)–C(4)	60.9
C(1)–C(2)–C(3)–C(5)	–7.2
C(2)–C(3)–C(4)–C(5)	–70.0
C(2)–C(3)–C(5)–C(6)	–2.7
C(3)–C(4)–C(5)–C(6)	71.7
C(3)–C(5)–C(6)–C(7)	–23.1
C(4)–C(5)–C(6)–C(7)	–89.3
C(5)–C(6)–C(7)–C(1)	56.1
C(5)–C(6)–C(7)–C(8)	176.0
C(6)–C(7)–C(1)–C(2)	–64.5
C(1)–C(7)–C(8)–C(9)	–46.0
C(6)–C(7)–C(8)–C(9)	–163.7
C(7)–C(8)–C(9)–C(10)	49.9
C(8)–C(9)–C(10)–C(11)	169.2
C(8)–C(9)–C(10)–C(14)	–56.0
C(9)–C(10)–C(11)–C(12)	164.3
C(14)–C(10)–C(11)–C(12)	45.0
C(9)–C(10)–C(14)–C(1)	62.2
C(9)–C(10)–C(14)–C(13)	–163.6
C(11)–C(10)–C(14)–C(1)	–174.6
C(11)–C(10)–C(14)–C(13)	–40.3
C(10)–C(11)–C(12)–C(13)	–32.5
C(11)–C(12)–C(13)–C(14)	6.5
C(12)–C(13)–C(14)–C(1)	148.2
C(12)–C(13)–C(14)–C(10)	20.9
C(10)–C(14)–C(1)–C(7)	49.0

the nature of the substituents.[7,11] In the present 2,9-dihydroxyverrucosane molecule, the formation of the *cis*-decalin system is probably precluded by the intramolecular overcrowding effect of C(4) and C(19).

Ring C adopts a slightly deformed chair conformation and the oxygen substituent O(2) is axial; atoms C(1), C(7), C(9), and C(10) are closely coplanar and atoms C(8) and C(14) are displaced by 0.55 and −0.71 Å from the plane. Since the displacement from an ideal chair conformation is ± 0.73 Å,[12] it appears that *trans*-fusion with ring B and the steric interaction between C(19) · · · O(2), 2.97 Å, induce appreciable flattening of this ring. The ring flattening is necessarily accompanied by a departure from the tetrahedral valency angles and the bond distances. The mean bond distance and intra-annular valency angle in this ring are 1.53 Å and 112°, respectively, but the bond distance, C(9)–C(10), 1.47 Å, and the angle C(7)–C(8)–C(9), 118°, are considerably shorter and larger than the mean values. On the other hand, two axial methyl bonds, C(7)–C(19), 1.58, and C(10)–C(20), 1.56 Å, which are in angular positions, are larger than the expected values.

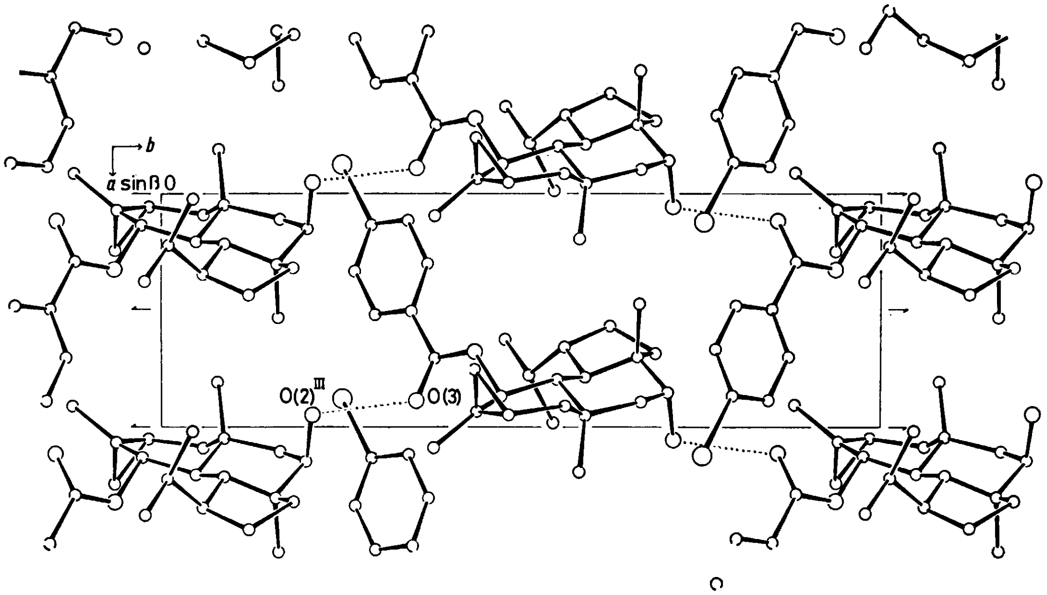

FIGURE 2 The molecular packing arrangement projected along the *c* axis: III, $2 - x, y - \frac{1}{2}, 1 - z$

The cyclopentane ring D, which is *anti-trans*-fused to ring C, has a conformation somewhere between a half-chair and β-envelope. This is evident from the torsion angles and the displacements of C(10) and C(11) from the C(12)—(14) plane (by 0.53 and −0.18 Å). Recently, Altona *et al.* reported that the conformation of the five-membered ring may be characterized more quantitatively by the values of the ' puckering angle ' ϕ_m, and the ' phase angle ' δ.[13] The calculated values, ϕ_m 45.5° and δ 18.3° for 2,9-dihydroxyverrucosane, coincide with the expected values in the conformation between a half-chair and β-envelope. The bond angles within the five-membered ring are as expected; maximum distortion of the bond angles occurs at C(11)–C(10)–C(14), 100°. This value shows the strain imposed at the C/D junction. It also supposes that the bulky isopropyl substituent at C(13) possibly plays an important role in determining the conformation of ring D. Indeed, the isopropyl group approaches O(1) from its hydrogen side [C(12) · · · C(16), 3.07, and C(12) · · · C(17), 3.09 Å], and the non-bonded contact between O(1) and C(15), 3.27 Å, causes the enlargement of the bond angle C(14)–C(13)–C(15) to 116°.

The bond distances in the *p*-bromobenzoate group are as expected: C–C ring system 1.39, C–C single bond 1.48, C–O 1.30, C=O 1.23, and Br–C 1.84 Å. These distances are in good agreement with those found in other *p*-bromobenzoate groups.[14] The mean intra-annular angle is 120° and the angles around C(21) appear to be normal. The *p*-bromobenzoate ester is not completely planar and the dihedral angle between the benzene plane and the C(22),C(21),O(3),O(1) plane is 11°. As usually occurs in esters,[15] the atom C(2) is coplanar with the carboxy-group and the resulting close contact between O(3) and C(2), 2.72 Å, indicates that the C=O bond is close to *syn*-planar with the C(2)–H(2) bond and the ester plane is tilted *ca.* 18° towards C(3) [O(3) · · · C(1), 4.08, and O(3) · · · C(3), 3.25 Å].

TABLE 6

Intermolecular distances (⩽ 3.6 Å)

$O(3) \cdots O(2^{III})$	2.91	$C(23) \cdots O(3^{I})$	3.51
$C(20) \cdots O(2^{I})$	3.38	$C(24) \cdots O(3^{I})$	3.27
$C(21) \cdots O(2^{III})$	3.60	$C(25) \cdots C(8^{II})$	3.58

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

I $x - 1, y, z$
II $1 - x, y - \frac{1}{2}, 1 - z$
III $2 - x, y - \frac{1}{2}, 1 - z$

The molecular packing arrangement projected along the *c*-axis is illustrated in Figure 2. Along the *b* axis, each molecule is linked by an intermolecular hydrogen bond [O(3) · · · O(2)^{III}, 2.91 Å]. All intermolecular distances were calculated, and most significant contacts ($\leqslant$3.6 Å) are given in Table 6. The molecular packing is efficient with several contacts approaching the sum of the van der Waals radii: the shortest non-hydrogen contact is C(24) · · · O(3)^{I}, 3.27 Å.

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