

Structures of Pertilide and Dibromocyclopertilide

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Abstract. Pertilide (I), $C_{15}H_{16}O_4$, m.p. 459–460 K (dec.), $\alpha_D^{20} = +1.4^\circ$ (chloroform, $c = 15.0 \text{ g dm}^{-3}$), orthorhombic, $P2_12_12_1$, $a = 8.278(4)$, $b = 25.244(12)$, $c = 6.179(3) \text{ \AA}$, $Z = 4$, $D_x = 1.339 \text{ g cm}^{-3}$, $\mu(\text{Cu } K\alpha) = 9.3 \text{ cm}^{-1}$. Dibromocyclopertilide (II), $C_{15}H_{16}Br_2O_4$, m.p. 524–525 K (dec.), orthorhombic, $P2_12_12_1$, $a = 14.655(7)$, $b = 16.089(8)$, $c = 6.558(3) \text{ \AA}$, $Z = 4$, $D_x = 1.805 \text{ g cm}^{-3}$, $\mu(\text{Cu } K\alpha) = 71.3 \text{ cm}^{-1}$. The final R values for (I) and (II) are 0.083 and 0.078 for 1161 and 1507 reflections, respectively. The chemical structures of pertilide (I) and dibromocyclopertilide (II) have been established as [1(10)Z,4E]-(3R,7R,8S)-germacra-1(10),4,11(13)-triene-12,8:14,3-diolide and (1S,3R,4S,5R,7R,8S,10S)-1,4-dibromocyclo-11(13)-ene-12,8:14,3-diolide.

Introduction. Pertilide is a germacrane sesquiterpene dilactone which was isolated from the leaves of *Pertya glabrescens* Sch. Bip. (Compositae). The chemical and spectroscopic studies led to the proposal of the chemical structure formulated as (I) (Fig. 1), but the stereochemistry could not be determined (Nagumo, Nagai & Inoue, 1980). X-ray structure analyses of (I) and (II) have been undertaken in order to establish the chemical structures, including their absolute configuration.

Crystals of (I) were grown in an acetone–diisopropyl ether solution as colorless prisms elongated along the c axis. The size of the X-ray specimen was about $0.1 \times 0.08 \times 0.4 \text{ mm}$. Prismatic crystals of (II),

obtained by the bromination of (I) in chloroform, were grown in an acetone solution. The X-ray specimen was about $0.12 \times 0.07 \times 0.5 \text{ mm}$. The lattice constants and intensity data were collected on a Philips PW 1100 diffractometer using Cu $K\alpha$ radiation monochromated by a graphite plate. A total of 1161 independent reflections [above the $2\sigma(I)$ level] of (I) were measured within a 2θ range of $6\text{--}152^\circ$; 2166 reflections were measured with 2θ $6\text{--}120^\circ$ for (II), 409 being equivalent and 250 being Friedel reflections. The R factors for these two types of reflections against the hkl set were 1.63 and 6.4%, respectively, indicating the effect of the anomalous dispersion of Br atoms. Intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied.

The crystal structure of (I) was solved by the direct method and that of (II) by the heavy-atom method. In both cases, the refinement was carried out by the block-diagonal least-squares method using *HBL5 IV* (Okaya & Ashida, 1967). A final R factor of 8.3% was obtained for (I), including anisotropic thermal parameters but not H-atom contributions. To determine the absolute configuration, the crystal structure of (II) was at first refined with anisotropic thermal parameters to an R value of 8.2% excluding H atoms, and then anomalous-dispersion corrections were applied to the Br atoms. The R factor for 1507 reflections was 7.8% when the correct set was chosen, while this value increased to 8.7% for the antipodal structure. Furthermore, a comparison between the observed and calculated intensity ratios of $I(hkl)/I(\bar{h}\bar{k}\bar{l})$ gave a consistent result. The final atomic parameters for (I) and (II) are listed in Table 1.*

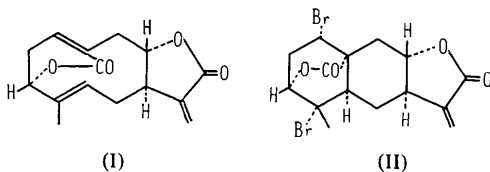


Fig. 1. Chemical formulae of pertilide (I) and dibromocyclopertilide (II).

* Lists of structure factors and anisotropic temperature factors for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36626 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic parameters ($\times 10^4$, for Br $\times 10^5$) and equivalent isotropic thermal parameters, with estimated standard deviations in parentheses, for pertilide (I) and dibromocycloperilide (II)

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq} (\AA^2)
Compound (I)				
C(1)	5148 (8)	7114 (2)	581 (10)	3.14 (0.08)
C(2)	6181 (10)	7432 (2)	2114 (11)	2.50 (0.10)
C(3)	6438 (8)	7077 (3)	4115 (10)	2.65 (0.09)
C(4)	7164 (7)	6541 (2)	3507 (11)	1.62 (0.08)
C(5)	6401 (8)	6089 (2)	4099 (10)	2.15 (0.08)
C(6)	6519 (7)	5555 (2)	3033 (11)	2.37 (0.09)
C(7)	4895 (7)	5480 (2)	1829 (10)	2.21 (0.07)
C(8)	4685 (7)	5863 (2)	-140 (9)	2.15 (0.07)
C(9)	3402 (7)	6304 (2)	80 (11)	2.07 (0.07)
C(10)	4095 (8)	6752 (2)	1385 (10)	2.30 (0.07)
C(11)	4723 (7)	4940 (2)	776 (10)	2.73 (0.08)
C(12)	4310 (7)	5010 (3)	-1545 (12)	2.62 (0.08)
C(13)	4863 (9)	4455 (3)	1676 (14)	4.92 (0.10)
C(14)	3711 (9)	6786 (2)	3741 (11)	3.24 (0.08)
C(15)	8600 (9)	6566 (3)	2028 (15)	5.40 (0.13)
O(1)	4831 (5)	7003 (2)	5061 (7)	2.47 (0.06)
O(2)	4196 (5)	5532 (1)	-1959 (7)	2.38 (0.06)
O(3)	4125 (6)	4680 (2)	-2929 (8)	2.76 (0.08)
O(4)	2423 (6)	6652 (2)	4480 (8)	3.82 (0.07)
Compound (II)				
Br(1)	56400 (12)	37575 (8)	82082 (31)	6.54 (0.02)
Br(2)	29928 (13)	8615 (15)	45031 (40)	4.77 (0.04)
C(1)	4799 (8)	2814 (7)	8053 (23)	5.15 (0.18)
C(2)	3852 (9)	3121 (10)	7289 (32)	7.50 (0.25)
C(3)	3506 (10)	2485 (11)	5756 (28)	7.80 (0.25)
C(4)	3516 (8)	1626 (9)	6660 (28)	5.37 (0.22)
C(5)	4500 (7)	1337 (6)	7045 (20)	3.61 (0.16)
C(6)	4629 (7)	901 (7)	9154 (19)	4.06 (0.15)
C(7)	5649 (7)	678 (6)	9193 (18)	3.19 (0.14)
C(8)	6199 (7)	1472 (7)	9167 (19)	3.57 (0.14)
C(9)	6153 (7)	1855 (6)	7058 (19)	4.42 (0.14)
C(10)	5159 (7)	2114 (6)	6726 (18)	4.63 (0.13)
C(11)	6056 (9)	269 (7)	11054 (21)	3.94 (0.16)
C(12)	7040 (9)	545 (7)	10963 (25)	5.08 (0.19)
C(13)	5743 (13)	-247 (10)	12433 (29)	6.58 (0.27)
C(14)	5025 (10)	2365 (8)	4522 (22)	5.45 (0.21)
C(15)	2829 (11)	1562 (11)	8525 (33)	9.95 (0.31)
O(1)	4131 (8)	2516 (7)	4022 (16)	6.00 (0.17)
O(2)	7126 (5)	1206 (4)	9740 (15)	3.74 (0.12)
O(3)	7693 (7)	278 (7)	11900 (22)	6.67 (0.20)
O(4)	5630 (8)	2428 (7)	3302 (14)	7.33 (0.18)

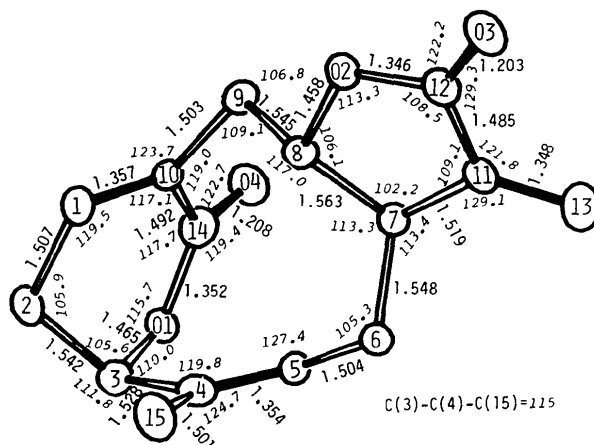


Fig. 2. The molecular structure of (I). Double bonds are indicated by filled bonds. Bond lengths (\AA) and angles ($^\circ$) are shown. The mean values of the e.s.d.'s are: $\sigma(\text{C}-\text{C}) = 0.009$, $\sigma(\text{C}-\text{O}) = 0.008$ \AA , and $\sigma(\text{C}-\text{C}-\text{C}) = 0.5$, $\sigma(\text{C}-\text{C}-\text{O}) = 0.5$, $\sigma(\text{O}-\text{C}-\text{O}) = 0.6^\circ$, $\sigma(\text{C}-\text{O}-\text{C}) = 0.5^\circ$.

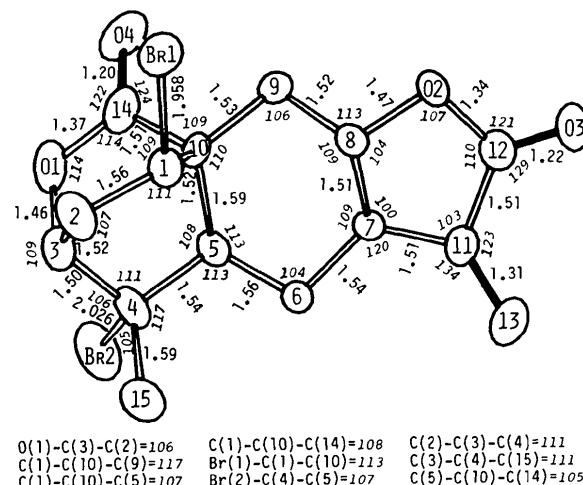


Fig. 3. The molecular structure of (II). Double bonds are indicated by filled bonds. The bond lengths (\AA) and angles ($^\circ$) are shown. The mean values of the e.s.d.'s are: $\sigma(\text{C}-\text{C}) = 0.019$, $\sigma(\text{C}-\text{O}) = 0.017$, $\sigma(\text{C}-\text{Br}) = 0.014$ \AA , and $\sigma(\text{C}-\text{C}-\text{C}) = 1.0$, $\sigma(\text{C}-\text{C}-\text{O}) = 1.1$, $\sigma(\text{O}-\text{C}-\text{O}) = 1.3$, $\sigma(\text{C}-\text{O}-\text{C}) = 1.1$, $\sigma(\text{C}-\text{C}-\text{Br}) = 0.9^\circ$.

Discussion. The absolute configuration of dibromocycloperilide (II) was determined and is as shown in Fig. 3. From the above result and chemical correlation, the structure of pertilide (I) including the absolute configuration was established as [1(10)*Z*,4*E*]- (3*R*,7*R*,8*S*)-germacra-1(10),4,11(13)-triene-12,8:14,3-diolide, as shown in Fig. 2. The bond lengths and angles for (I) and (II) are given in Figs. 2 and 3. The values are consistent with the chemical structures in Fig. 1.

The *trans,trans*-cyclodeca-1,5-diene ring of (I) adopts a unique conformation in which C(14) and C(15) are arranged *anti* with respect to the ring plane.

The two double bonds of the above ten-membered ring seem to be in close contact, as shown in Fig. 4 (center-to-center distance: 2.94 \AA). The deviations of C(1), C(4), C(5) and C(10) from the best plane through these atoms are within 0.08 \AA , and hence the best plane through the double bonds C(1)-C(10) and C(4)-C(5) has good planarity; it is more planar than those through each double bond, thus the torsion angles C(2)-C(1)-C(10)-C(9) and C(3)-C(4)-C(5)-C(6) are -160 and $+155^\circ$ respectively, and the *trans* double bonds in the ten-membered ring have some strain. From the above-mentioned facts, some π - π interaction is expected.

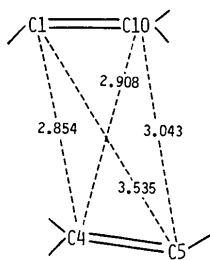


Fig. 4. Interatomic distances (Å) between the C—C double bonds in molecule (I). The mean e.s.d. of the values shown is $\sigma(C \cdots C) = 0.009$ Å.

The three condensed six-membered rings of (II) adopt slightly deformed boat forms, the centered six-membered ring is a chair, and the γ -lactone ring shows an envelope form, while the γ -lactone ring of (I) is much more planar than that of (II). The junctions

between the ten-membered ring and the γ -lactone ring, for (I), and the six-membered ring and the γ -lactone ring, for (II), are all *trans*. In both crystals, the molecules are packed together mainly by van der Waals forces and there are no hydrogen bonds.

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Diethyl Terephthalate

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Abstract. $C_{12}H_{14}O_4$, $M_r = 222.24$, monoclinic, $P2_1/n$ (systematic absences: $h0l$, $h + l$ odd; $0k0$, k odd), $a = 9.140$ (1), $b = 15.450$ (3), $c = 4.225$ (6) Å, $\beta = 92.89$ (1)°, $U = 595.9$ Å³; $Z = 2$, $D_x = 1.238$, $D_m = 1.243$ Mg m⁻³, m.p. = 317 K. $R = 0.065$ for 922 counter reflexions. $C(4)=O(8) = 1.206$ (2) Å and the ethyl $C(6)-C(7) = 1.467$ (2) Å.

Introduction. This work is a continuation of our investigation of the model compounds of poly(ethylene terephthalate) (Hašek, Ječný, Langer, Huml & Sedláček, 1980). The structure of diethyl terephthalate was determined by Bailey (1949) with a relatively high $R = 0.28$. In order to obtain more reliable results for the discussion of IR spectra, we redetermined this structure.

The unit-cell parameters were obtained by refinement of 19 reflexions with $23 < 2\theta < 112^\circ$ measured with a Syntex $P2_1$ diffractometer. X-ray intensities were collected by $\theta-2\theta$ scans at room temperature using monochromated Cu $K\alpha$ radiation. 1005 independent reflexions were measured up to $\sin \theta/\lambda = 0.59$ Å⁻¹; 83 of them were classified as unobserved with $I < 1.96\sigma_I$, where σ_I was calculated from counting statistics.

No correction was made for absorption or extinction [$\mu(\text{Cu } K\alpha) = 0.73$ mm⁻¹, crystal dimensions $0.1 \times 0.1 \times 0.2$ mm]. Other measurement details are the same as in Hašek, Hlavatá & Huml (1977).

The structure was redetermined by direct methods with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by least squares in the block-diagonal approximation. The function minimized was $\sum w\Delta^2$, where $w = [\sigma_F^2 + (0.02F)^2]^{-1}$ and $\Delta = |F_o| - |F_c|$. Atomic scattering factors were taken from *International Tables for X-ray*

Table 1. *Final fractional coordinates* ($\times 10^4$) *and* B_{eq} *values* (Å²) *of the non-H atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq}
C(1)	1503 (2)	-102 (1)	9883 (4)	6.42 (4)
C(2)	-689 (2)	703 (1)	8576 (4)	6.49 (4)
C(3)	811 (2)	615 (1)	8426 (4)	5.85 (4)
C(4)	1643 (2)	1280 (1)	6715 (4)	6.19 (4)
O(5)	3068 (1)	1106 (1)	6724 (3)	6.90 (3)
C(6)	3998 (2)	1718 (1)	5110 (5)	7.42 (5)
C(7)	5484 (3)	1357 (2)	5184 (7)	9.69 (8)
O(8)	1082 (2)	1901 (1)	5419 (4)	8.34 (4)