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(4*RS*,5*SR*)-2,5-Di-*tert*-butyl-4,5-dihydroxy-4-methyl-2-cyclopenten-1-one, an Unusual Product of Oxidation of 2,6-Di-*tert*-butyl-4-methylphenol[*]

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Abstract. $C_{14}H_{24}O_3$, orthorhombic, $Pna2_1$, a = 21·171 (3), b = 10·415 (2), c = 6·359 (1) Å [at 295–297 K, based on λ(Cu $K\alpha$) = 1·5418 Å], Z = 4, ρ_{calc} = 1·105 Mg m^{-3}; structure based on 1278 $|F_o|^2$ values, $R(F)$ = 0·029, $R(F^2)$ = 0·042, σ_1 = 1·547. X-ray analysis has identified the compound and specified the relative stereochemical configuration. The cyclopentene ring has the envelope conformation, atom C(5) defining the flap. Bond C(4)–C(5) is abnormally long, 1·574 (2) Å, and angles O(4)–C(4)–C(5) and C(11)–C(5)–C(4) are abnormally large, 116·5 (1) and 117·0 (1)° respectively; these features are consistent with the fact that the conformation around ring bond C(4)–C(5) is only ~26·5° from eclipse, which implies considerable repulsion, especially between the 4-hydroxyl and 5-*tert*-butyl groups. The bond to the 5-*tert*-butyl group is also long, 1·576 (3) Å. Two kinds of H-bonds, one bifurcated (intra- and intermolecular) and very weak, join the molecules into ribbons two-molecules wide running parallel to **c** and held together in a herringbone pattern by van der Waals forces.

Introduction. In model oxidation studies (Benjamin, Raaen, Hagaman & Brown, 1978) relating to the problem of coal structure, the common antioxidant 2,6-di-*tert*-butyl-4-methylphenol, known to occur in brown coals, was oxidized with permanganate under carefully controlled conditions. Most of the products were identified from elemental analyses and from infrared and NMR spectra; however, two of the products required single-crystal X-ray analyses for identification. The present report concerns the structure of the product $C_{14}H_{24}O_3$, which was inferred by Benjamin *et al.* (1978) to be a racemic form of either 2,5-di-*tert*-butyl-4,5-dihydroxy-4-methyl-2-cyclopenten-1-one (1) or its isomer 2,4-di-*tert*-butyl-4,5-dihydroxy-5-methyl-2-cyclopenten-1-one (2). A decision between (1) and (2) could not be made from the NMR data.

A specimen ~0·2 × 0·2 × 0·7 mm was cut from a larger crystal. The systematic absences were those of space groups $Pna2_1$ and $Pnam$ (alternative orientation for $Pnma$). Group $Pnam$ was excluded on the basis of its multiplicity of general equipoints, the cell volume, and the asymmetry of (1) and (2) (also on the basis of intensity statistics). The cell parameters (see *Abstract*) were determined by the least-squares method from diffractometer angle data for 14 reflections (55° < 2θ < 96°). Mosaic spreads of ~1° (full width at background) necessitated use of the triple ω-scan technique invented by Levy (1966) [see also Einstein (1974)], as used for crystals of similar mosaicity (Brown & Strydom, 1974; Brown, Pinson & Ingram, 1979). A total of 1314 independent intensities were recorded ($2\theta \le 130°$, Cu $K\alpha$ radiation). Absorption correction factors on $|F_o|^2$ ranging from 1·114 to 1·247 were calculated by Gaussian integration (Busing & Levy, 1957) (μ = 0·574 mm^{-1}). The statistical variances of the $|F_o|^2$ data were adjusted empirically by the addition of the term $(0{\cdot}4|F_o|^2)^2$. The weights used later in least-squares refinement on the $|F_o|^2$ data were the reciprocals of the adjusted variances.

The structure solution was obtained by use of the 198 E's ≥ 1·40 and the direct-method program *MULTAN* (Main, Woolfson & Germain, 1971), the indicated best set of phases yielding the 17 C and O

Table 1. *Coordinates of the carbon and oxygen atoms*

	x	y	z
C(1)	0·15890 (8)	0·34221 (18)	0·19646[*]
C(2)	0·19977 (7)	0·36265 (15)	0·01061 (40)
C(3)	0·16391 (8)	0·41794 (17)	−0·13559 (39)
C(4)	0·09793 (7)	0·45096 (17)	−0·06359 (40)
C(5)	0·08941 (8)	0·35741 (17)	0·12882 (38)
C(6)	0·27005 (8)	0·33295 (18)	0·00155 (44)
C(7)	0·29493 (10)	0·35338 (27)	−0·22127 (50)
C(8)	0·28130 (11)	0·19399 (23)	0·06566 (56)
C(9)	0·30452 (11)	0·42294 (29)	0·15301 (57)
C(10)	0·09644 (10)	0·59032 (18)	0·00772 (49)
C(11)	0·05881 (9)	0·22246 (18)	0·08240 (44)
C(12)	0·09269 (11)	0·15036 (23)	−0·09313 (60)
C(13)	−0·01129 (10)	0·23863 (26)	0·02222 (58)
C(14)	0·06130 (15)	0·14138 (28)	0·28362 (63)
O(1)	0·17478 (6)	0·32407 (17)	0·37798 (38)
O(4)	0·05620 (6)	0·43267 (13)	−0·23653 (37)
O(5)	0·05473 (6)	0·41755 (14)	0·29471 (38)

[*] This coordinate was held fixed in the refinement.

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atoms as the highest peaks of the *E* map. Full-matrix least-squares refinement was started at once. The 24 H atoms were located in a difference Fourier map at an early stage, and their coordinates and isotropic thermal parameters were thereafter included among the parameters adjusted. In the final refinement (see *Abstract* for the indicators of goodness of fit), the 36 reflections having $2\theta < 30°$ were given zero weights because their background measurements were unreliable. Extinction corrections were not required. A final difference map showed densities from $-0{\cdot}14$ to $+0{\cdot}13$ e Å^{-3}. The C and O scattering factors used were from *International Tables for X-ray Crystallography* (1962), and those for H were from Stewart, Davidson & Simpson (1965). The atomic coordinates of the C and O atoms are given in Table 1.*

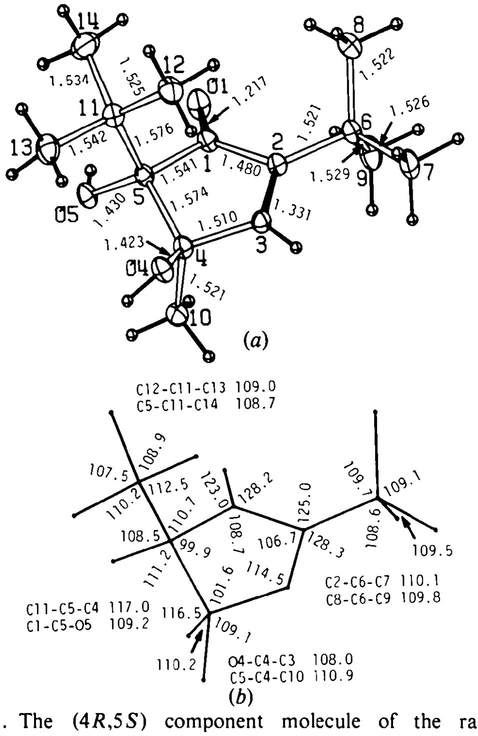

Fig. 1. The (4*R*,5*S*) component molecule of the racemate (4*RS*,5*SR*)-2,5-di-*tert*-butyl-4,5-dihydroxy-4-methyl-2-cyclopenten-1-one. (*a*) O and C atoms are represented by their thermal ellipsoids of 20% probability. The individual ellipsoids are labelled, only numerals being used for the C atoms. H atoms are represented by the small unlabelled spheres of arbitrary radius. The two double bonds are black. The numbers attached to the C–C and C–O bonds are bond lengths (Å), whose estimated standard errors are all in the range 0·002–0·004 Å. (*b*) Skeletal drawing with H atoms omitted (same view direction as in *a*). The numbers on the drawing are the valence angles (°), whose estimated standard errors are in the range 0·1–0·2°.

Discussion. The compound is the racemate of (1) specified by the prefix (4*RS*,5*SR*) in the title. The relative stereochemical configuration (see Fig. 1) is specified more simply by the name (±)-2,5-di-*tert*-butyl-*trans*-4,5-dihydroxy-4-methyl-2-cyclopenten-1-one.

The ring has the envelope conformation to be expected for a cyclopentene ring; atom C(5), across the ring from the C(2)–C(3) double bond, is 0·474 (3) Å from the best least-squares plane through the other ring atoms, none of which is more than 0·025 (1) Å from the plane. The ring torsion angles, for the bonds in the order C(1)–C(2), C(2)–C(3), *etc.*, are 15·2 (2), 4·7 (2), −21·7 (2), 27·5 (2), and −27·0 (2)°; other torsion angles have been deposited.*

Bond lengths and valence angles not involving H atoms are shown in Fig. 1. The unusual ones have been noted in the *Abstract*. The apparent C–H bond lengths (individual e.s.d.'s ~0·02–0·04 Å) range from 0·88 to 1·05 Å, averaging 0·97 Å; the O–H bond lengths are

Table 2. *Geometry of the hydrogen bonding*

The symmetry operations are: (i) $\bar{x}, \bar{y}+1, z-\frac{1}{2}$; (ii) $x, y, z+1$.

Hydrogen bond O–H···O	Distances (Å) O–H	H···O	O···O	Angle (°) O–H···O
O(4)–H(23)···O(5^{i})	0·86 (3)	1·98 (3)	2·826 (2)	169 (3)
O(5)–H(24)···O(1)	0·83 (3)	2·32 (3)	2·773 (2)	115 (3)
O(5)–H(24)···O(4^{ii})		2·31 (4)	2·985 (2)	139 (2)

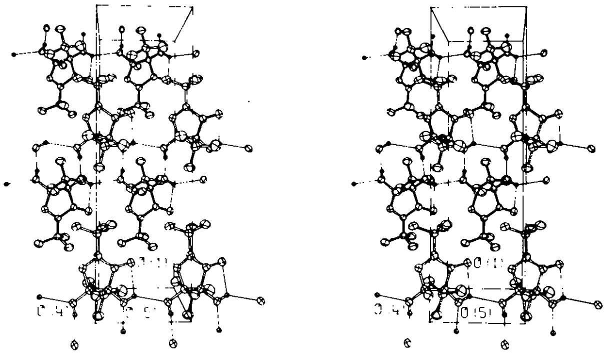

Fig. 2. Stereoscopic drawing showing the molecular packing and hydrogen bonding in crystalline (4*RS*,5*SR*)-2,5-di-*tert*-butyl-4,5-dihydroxy-4-methyl-2-cyclopenten-1-one. The C and O atoms are represented by their ellipsoids of 20% probability; of the H atoms, only those of hydroxy groups are shown (as small spheres). The single-line bonds indicate the H···O H-bond interactions. The direction **a** is along the vertical from bottom to top; **c** is horizontal from left to right. The cell outline shown is centered at the point $\frac{1}{2},0,\frac{1}{2}$.

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* Lists of structure factors, anisotropic thermal parameters for the C and O atoms, coordinates and isotropic thermal parameters for the H atoms, and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34597 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

included in Table 2, which gives the detailed geometry of the hydrogen bonding.

The hydrogen bonding is shown in the packing drawing of Fig. 2. Each molecule is linked by a very weak hydrogen bond (half of a bifurcated bond) from its O(5) hydroxyl to the O(4) hydroxyl oxygen of the translation-equivalent molecule in the adjacent cell along **c**, resulting in H-bonded molecular chains along **c**. The other branch of the bifurcated bond is intramolecular, between the O(5) hydroxyl and the carbonyl oxygen, O(1). Each of the H-bonded chains is further connected by O(4)—H(4)···O(5) H-bonds to the equivalent chain related to it by a 2_1 screw axis parallel to **c**. The result is the ribbon structure noted in the *Abstract*.

The computer programs used in this study and not specifically referenced are the same as those used for the corresponding calculations of Lisensky, Johnson & Levy (1976).

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Conformation of *cyclo*(-L-Leu-L-Phe-Gly-D-Leu-D-Phe-Gly-) Dihydrate

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Abstract. $C_{34}H_{46}N_6O_6.2H_2O$, triclinic, $P\bar{1}$, $a = 8\cdot599\,(3)$, $b = 16\cdot825\,(9)$, $c = 6\cdot136\,(2)$ Å, $\alpha = 92\cdot38\,(3)$, $\beta = 95\cdot85\,(3)$, $\gamma = 87\cdot14\,(4)^\circ$, $V = 881\cdot4$ Å^3 at 138 ± 2 K and $a = 8\cdot701\,(3)$, $b = 16\cdot948\,(7)$, $c = 6\cdot172\,(9)$ Å, $\alpha = 93\cdot65\,(7)$, $\beta = 96\cdot29\,(7)$, $\gamma = 85\cdot78\,(3)^\circ$, $V = 900\cdot8$ Å^3 at 295 K, $Z = 1$, $D_x = 1\cdot236$, $D_m = 1\cdot241$ Mg m^{-3}. The molecule possesses a center of symmetry and contains two equivalent intramolecular NH···O hydrogen bonds (3·04 Å). The structure was obtained from 3639 reflections measured at 138 ± 2 K using Cu $K\bar{\alpha}$ radiation and refined to a final R factor of 0·068 for 2366 reflections used in the least-squares calculation (0·112 for all reflections).

Introduction. *cyclo*(-L-Leu-L-Phe-Gly-D-Leu-D-Phe-Gly-) is one of the series of cyclo-isomeric hexapeptides containing two residues of glycine, two of leucine and two of phenylalanine, synthesized by Bláha (1972). The peptide is a *meso* form and possesses a potential center of symmetry. The structure investigation was undertaken as part of our overall program to study the conformational features of cyclic peptides and the stereochemistry of cyclic isomers.

Crystals of the compound were obtained by evaporation from methanol solution at room temperature. The thin plate-shaped crystals showed large mosaic spreads ranging from 2 to 4°. A crystal 0·35 × 0·13 × 0·04 mm and with a mosaic spread of about 2° was selected for all measurements.

Photographic investigations showed the crystal to be triclinic. The intensity statistics: $|\bar{E}| = 0\cdot848$ and $\overline{|E^2 - 1|} = 0\cdot894$, were not conclusive, but an $N(z)$ test clearly indicated the centrosymmetric space group $P\bar{1}$. Refinement in $P1$ yielded no improvement in the R value and only a 0·5% decrease in the value for $\sum W||kF_o| - |F_c||^2$ over the refinement in $P\bar{1}$ and, therefore, all final results were evaluated according to the latter space group. The unit-cell parameters and intensity data were obtained at 138 K with a CAD-4 automatic diffractometer controlled by a PDP8/e computer and fitted with a low-temperature apparatus. The cell parameters were determined by a least-squares refinement of $+2\theta$ and -2θ values of 23 reflections measured with Cu $K\alpha_1$ ($\lambda = 1\cdot54051$ Å) radiation.

Intensities of all independent reflections with $2\theta \leq 150^\circ$ were measured employing the θ–2θ scan tech-

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