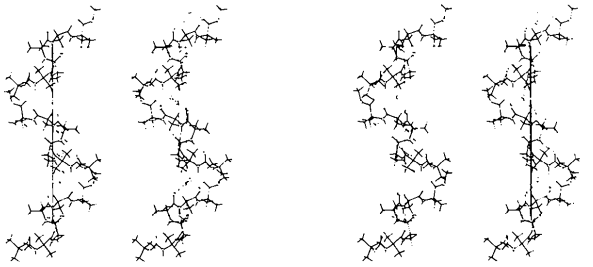

Fig. 3. Stereoscopic view of the molecular packing. Hydrogen bonds are indicated as dashed lines.

Indeed, the bond angles β and δ of the title compound are significantly less whereas ε and η tend to be greater than the tetrahedral value. The bond lengths do not show significant deviations from ideal peptide geometry.

Three intramolecular hydrogen bonds in accordance with type III β-turns (right-handed helical conformation) are observed: N(3)···O(2) 2·95 (1) Å, N(4)···O(3) 2·95 (1) Å and N(5)···O(4) 3·01 (1) Å.

The pentapeptide molecules are connected head-to-tail along [001] by a system of intermolecular hydrogen bonds: One hydrogen bond connects directly two peptide molecules [N(1)···O(6′) 3·13 (1) Å; symmetry code: $\frac{1}{2}-x$, $2-y$, $-\frac{1}{2}+z$]. The two water molecules [O(9) and O(10)], which fill the space between the head-to-tail connexion, are used for a 'long-range' bridge between N(2) and O(5′) [N(2)···O(9′) 2·91 (1) Å; symmetry code: $\frac{1}{2}-x$, $2-y$, $-\frac{1}{2}+z$; O(9)···O(10′) 2·74 (1) Å; symmetry code: $-1+x$, y, z; and O(10)···O(5) 2·83 (1) Å]. Finally there is a hydrogen bond between O(9) and O(6), which is bifurcated at the carbonyl O atom [O(9)···O(6) 2·95 (1) Å]. Fig. 3 shows that the head-to-tail connexion of the 3_{10}-helices leads to left-handed 'superhelices' along [001]. The latter are held together by hydrophobic interactions. It is of particular interest that these superhelices have a parallel packing in contrast to the antiparallel packing of the α-helices of the undecapeptide Boc-L-Ala-Aib-Ala-Aib-Ala-Glu(OBzl)-Ala-Aib-Ala-Aib-Ala-OMe (Butters, Hütter, Jung, Pauls, Schmitt, Sheldrick & Winter, 1981; Schmitt, Winter, Bosch & Jung, 1982).

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Structure of the Monoclinic Form of 2,6-Di-*tert*-butyl-4-methylphenol (DBMP), $C_{15}H_{24}O$

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Abstract. $M_r = 220{\cdot}34$, monoclinic, $C2/c$, $a = 25{\cdot}810$ (9), $b = 8{\cdot}488$ (1), $c = 16{\cdot}481$ (7) Å, $\beta = 129{\cdot}45$ (2)°, $U = 2788$ (1) Å^3, $Z = 8$, $D_x = 1{\cdot}050$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ (Mo $K\alpha$) = 0·059 mm^{-1}, $T = 288$K, $F(000) = 976$, final $R = 0{\cdot}041$ for 1164 unique reflections. Some of the bond angles

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involving the *tert*-butyl groups deviate significantly from standard values to avoid intramolecular crowding.

Introduction. Recently, DBMP, which is widely used as an antioxidant in food, has been shown to have a wide variety of biological activities, *i.e.* inhibition of the mutagenicity of benzo[*a*]pyrene (Calle, Sullivan, Nettleman, Ocasio, Blazyk & Jollick, 1978), inactivation of human and murine cytomegalovirus and Semliki Forest virus (Kim, Moon, Sapienza, Carp & Pullarkat, 1978), and stimulation of DNA synthesis (Larsen & Tarding, 1978). Takenaga, Honma & Hozumi (1981) and ourselves (Ohno, Asahi & Isono, 1982) have found that DBMP also has differentiation controlling activity for some leukemia cells. The orthorhombic crystal structure of DBMP was reported by Maze-Baudet (1973). Recently we found a new monoclinic crystalline form at low temperature.

Experimental. Single crystals were obtained as colorless plates (m.p. 342–343 K) from methanol–water at 253 K. Since the crystal sublimes easily, a plate crystal $0{\cdot}13 \times 0{\cdot}20 \times 0{\cdot}50$ mm was sealed in a thin-walled glass capillary. Systematic absences *hkl* with $h + k$ odd and *h*0*l* with *l* odd are consistent with space group *Cc* or *C*2/*c*; since this compound is optically inactive *C*2/*c* was adopted. Rigaku AFC four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; intensities of standard reflections $\bar{5}13$, $\bar{9}34$ and 602 constant during the experiment; $2\theta \leq 55°$; 1164 unique reflections obtained with the significance level $3{\cdot}0\,\sigma(F_o)$; 2038 unobserved reflections; Lorentz and polarization corrections, but no absorption correction. The structure was solved by means of the direct-methods program *MULTAN* (Main, Woolfson & Germain, 1971), which yielded all the C and O atoms; difference Fourier syntheses gave the positions of all the H atoms; structure refined by a block-diagonal least-squares method based on $|F_o|$, anisotropic temperature factors for all atoms, $R = 0{\cdot}041$ and $R_w = 0{\cdot}038$; unit weight given to all reflections; calculations carried out on the FACOM M-200 computer of this Institute using the *UNICS* III program system (Sakurai & Kobayashi, 1979); best-plane calculation made with the program *BP7A* (Ito, 1981); atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic coordinates are shown in Table 1.* The atomic numbering and thermal ellipsoids are shown in Fig. 1. The bond lengths, angles and torsion angles are given in Table 2. The main features of the molecular structure are identical with those reported by Maze-Baudet (1973): (1) the bond lengths in the benzene ring and the C–O distance are normal; (2) C(4)–C(15) = 1·505 (4) Å shows evidence of hyperconjugation between the methyl and the benzene ring; (3) some of the bond angles involving the *tert*-butyl groups are significantly different from the standard values. In particular, C(1)–C(2)–C(7) and C(1)–C(6)–C(11) are 122·4 (3) and 122·2 (3)°, respectively, and C(9)–C(7)–C(10) and C(12)–C(11)–C(13) are 106·8 (3) and 106·3 (3)°, respectively. These deformations seem to reduce the intramolecular crowding of the *tert*-butyl groups. Similar deformations were reported for 2,6-di-*tert*-butyl-4-methoxyphenol (Burton, Le Page, Gabe & Ingold, 1980). The *tert*-butyl groups are

Table 1. *Atomic coordinates with estimated standard deviations in parentheses*

Positional parameters are multiplied by 10^4. B_{eq} values are equivalent isotropic temperature factors.

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_j^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq} (Å²)
O	4425 (1)	3250 (3)	4773 (2)	5·2 (0·1)
C(1)	3939 (2)	2293 (4)	3951 (2)	3·2 (0·1)
C(2)	3769 (2)	883 (4)	4177 (2)	3·1 (0·1)
C(3)	3291 (2)	−65 (4)	3318 (2)	3·3 (0·2)
C(4)	2994 (2)	344 (4)	2292 (2)	3·5 (0·2)
C(5)	3169 (2)	1767 (4)	2119 (2)	3·4 (0·2)
C(6)	3637 (2)	2790 (4)	2923 (2)	3·1 (0·2)
C(7)	4080 (2)	401 (4)	5306 (2)	3·8 (0·2)
C(8)	3897 (2)	1624 (5)	5770 (3)	5·9 (0·2)
C(9)	3805 (2)	−1194 (5)	5322 (3)	5·7 (0·2)
C(10)	4841 (2)	219 (5)	5991 (3)	5·5 (0·2)
C(11)	3821 (2)	4362 (4)	2695 (3)	3·9 (0·2)
C(12)	3730 (2)	5767 (4)	3183 (3)	5·3 (0·2)
C(13)	3367 (2)	4687 (5)	1506 (3)	5·5 (0·2)
C(14)	4547 (2)	4296 (4)	3101 (3)	5·2 (0·2)
C(15)	2497 (2)	−733 (4)	1391 (3)	4·9 (0·2)

Table 2. *Intramolecular bond distances* (Å), *angles* (°) *and important torsion angles* (°) *with estimated standard deviations in parentheses*

O–C(1)	1·383 (3)	C(5)–C(6)	1·390 (4)
C(1)–C(2)	1·404 (5)	C(6)–C(11)	1·541 (5)
C(1)–C(6)	1·406 (5)	C(7)–C(8)	1·532 (7)
C(2)–C(3)	1·398 (4)	C(7)–C(9)	1·537 (6)
C(2)–C(7)	1·540 (5)	C(7)–C(10)	1·528 (5)
C(3)–C(4)	1·385 (5)	C(11)–C(12)	1·539 (7)
C(4)–C(5)	1·382 (5)	C(11)–C(13)	1·539 (5)
C(4)–C(15)	1·505 (4)	C(11)–C(14)	1·539 (7)
O–C(1)–C(2)	118·9 (3)	C(5)–C(6)–C(11)	121·6 (3)
O–C(1)–C(6)	117·9 (3)	C(2)–C(7)–C(8)	109·5 (3)
C(2)–C(1)–C(6)	123·3 (3)	C(2)–C(7)–C(9)	111·3 (3)
C(1)–C(2)–C(3)	116·4 (3)	C(2)–C(7)–C(10)	111·0 (4)
C(1)–C(2)–C(7)	122·4 (3)	C(8)–C(7)–C(9)	107·2 (4)
C(3)–C(2)–C(7)	121·2 (3)	C(8)–C(7)–C(10)	111·0 (3)
C(2)–C(3)–C(4)	122·7 (3)	C(9)–C(7)–C(10)	106·8 (3)
C(3)–C(4)–C(5)	118·1 (3)	C(6)–C(11)–C(12)	111·7 (4)
C(3)–C(4)–C(15)	121·1 (3)	C(6)–C(11)–C(13)	111·2 (3)
C(5)–C(4)–C(15)	120·9 (3)	C(6)–C(11)–C(14)	110·0 (3)
C(4)–C(5)–C(6)	123·3 (3)	C(12)–C(11)–C(13)	106·3 (3)
C(1)–C(6)–C(5)	116·2 (3)	C(12)–C(11)–C(14)	110·5 (3)
C(1)–C(6)–C(11)	122·2 (3)	C(13)–C(11)–C(14)	107·0 (4)
C(1)–C(2)–C(7)–C(8)	61·8 (5)	C(1)–C(6)–C(11)–C(12)	−55·6 (5)
C(1)–C(2)–C(7)–C(9)	−179·9 (4)	C(1)–C(6)–C(11)–C(13)	−174·2 (4)
C(1)–C(2)–C(7)–C(10)	61·1 (5)	C(1)–C(6)–C(11)–C(14)	67·5 (5)

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, torsion angles and best planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38411 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

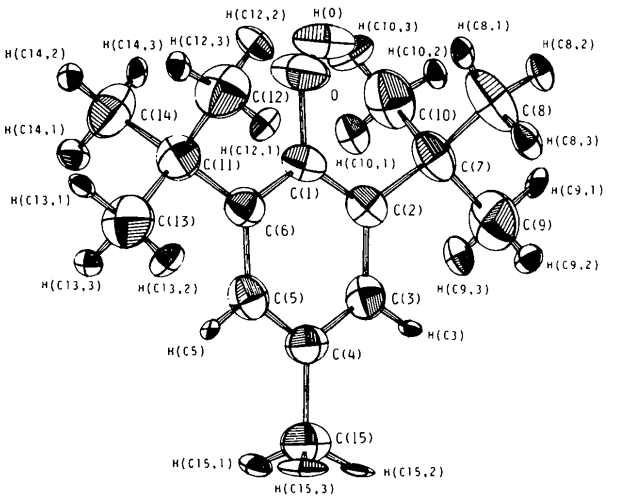

Fig. 1. Atomic numbering of the molecule. The thermal ellipsoids are at 50% probability for O and C, but at 10% probability for H.

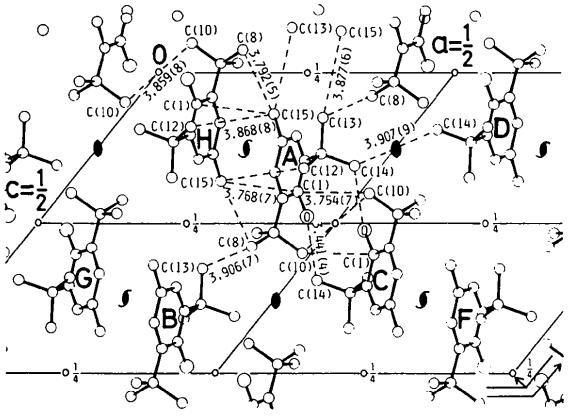

Fig. 2. The crystal structure projected along the *b* axis. Broken lines show the van der Waals contacts of atoms (distances in Å). Symmetry code: (*A*) *x*,*y*,*z*; (*B*) *x*,$-y$,$\frac{1}{2}+z$,; (*C*) $-x$,$-y$,$-z$; (*D*) $-x$,*y*,$-\frac{1}{2}-z$; (*E*) $\frac{1}{2}+x$, $\frac{1}{2}+y$, *z*; (*F*) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (*G*) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$; (*H*) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $-\frac{1}{2}-z$.

situated so that one of the methyl groups is near the benzene plane and the other two face the hydroxy group. A few degrees of rotation are allowed about the bond between a C atom in a benzene ring and the central atom of a *tert*-butyl group. The nearest-neighbor distance between the O atom and the H atoms of *tert*-butyl groups is O···H(C12,2) = 2·30 (4) Å. Some of the H coordinates in the Maze-Baudet result are not acceptable. The present analysis gives more reasonable positions. The H atoms belonging to the *tert*-butyl groups are all in ± *gauche* or *trans* positions. One of the H atoms [H(C15,2)] of the methyl group is near the plane of the benzene ring. The benzene ring is planar within 0·015 (5) Å, and O and C(15) are slightly above (*ca* 0·05 Å) and C(7) and C(11) are slightly below the benzene plane. The crystal structure projected along the *b* axis is shown in Fig. 2. Molecules are arranged in a plane parallel to $(\bar{1}01)$ with normal van der Waals distances.

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Structure of (2*R*,3*S*)-3,5-Dimethyl-2-{(*S*)-1-[(3*S*,5*R*,6*R*)-3,5-dimethyl-2-oxotetrahydro-2*H*-pyran-6-yl]ethyl}-2,3-dihydro-4-pyranone, $C_{16}H_{24}O_4$

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(*Received* 8 *December* 1982; *accepted* 9 *February* 1983)

Abstract. $M_r = 280·4$, monoclinic, $P2_1/n$, $a = 10·191$ (3), $b = 7·621$ (7), $c = 20·354$ (6) Å, $\beta = 94·47$ (2)°, $V = 1576$ (2) Å^3, $Z = 4$, $D_x = 1·18$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, $\mu = 0·078$ mm^{-1}, $F(000) = 608$, $T = 298$ K. Final $R = 0·042$ for 868 independent reflections. The tetrahydropyran-2-one ring has a chair conformation while the dihydropyran-4-one ring is in a twisted half-chair conformation.

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