

C8–C13 ring is reflected in a shortening of the C7–C8 bond and a lengthening of the C8–C9 and C8–C13 bonds.

The angle between the planes through the phenyl rings is 77.1° , and the dihedral angle C1–C6–C7–O20 is $74.0^\circ(4)$ (see Fig. 1). This rotation of a phenyl ring relative to the keto-group and to the other phenyl ring is much larger than the rotations found in benzophenone,⁷ 3,3'-dibromobenzophenone⁸ and 4,4'-dimethoxybenzophenone,⁹ where the angles between the phenyl rings and the plane defined by the atoms corresponding to C6, C7, C8 and O20 are about $25-35^\circ$, and the angles between the planes of the phenyl rings are about 55° . This large rotation must be a result of the *intra*-molecular crowding caused by the position of the large 3-methyl-2-butenyl group *syn* to O20 and also by the position of the hydroxyl group (O24) *syn* to the C1–C6 ring. A similar situation is found in the molecules of *syn*- and *anti*-4-bromobenzophenone oxime *O*-picryl ethers¹⁰ where the phenyl rings *syn* to the picryl groups are rotated $60-70^\circ$, relative to the plane through the oxime group, whereas the phenyl rings *anti* to the picryl groups are rotated only $18-23^\circ$.

The *inter*-molecular distances indicate two hydrogen bonds: one from O19 to O21 in position: $-0.5+x$, $-0.5+y, z$ distance: $2.797(4)$ Å; and one from O24 to O20 in position: $-0.5+x$, $0.5-y$, $-0.5+z$, distance: $2.732(3)$ Å.

Acknowledgement. The authors thank Professor K. Seff for the use of the X-ray diffraction equipment at the Chemistry Department, University of Hawaii.

1. Chang, B.-L. *M.S. Thesis*, School of Pharmacy, University of Mississippi, December 1976.
2. Ottersen, T. *LP-76 Computer Program*, *Cryst. Prog. Lib.*, Department of Chemistry, University of Hawaii.
3. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
4. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
5. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1968) 390.
6. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
7. Fleischer, E. B., Sung, N. and Hawkinson, S. J. *Phys. Chem.* 72 (1968) 4311.
8. Norment, H. G. and Karle, I. L. *Acta Crystallogr. B* 15 (1962) 873.
9. Patabhi, V. and Venkatesan, K. *J. Cryst. Mol. Struct.* 3 (1973) 25.
10. McCullough, J. D., Jr., Paul, I. C. and Curtin, D. Y. *J. Am. Chem. Soc.* 94 (1972) 883.
11. Manojlović, L. and Edmunds, I. G. *Acta Crystallogr. B* 13 (1965) 543.

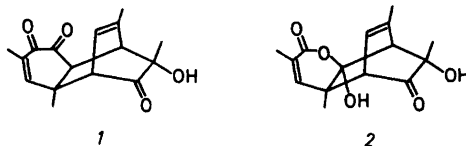
Received January 18, 1977.

On the Crystal Structure of 5,8-Etheno-3,4a,7,9-tetramethyl-4a,5,6,7,8,8a-hexahydrochromene-7,8a-diol-2,6-dione, Formed by Periodate Oxidation of 2,4-Dimethylphenol

BENGT KARLSSON,^a BENGT O. LINDGREN,^b
ANNE-MARIE PILOTTI^a and
ANNE-CHARLOTTE SÖDERHOLM^a

^a Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden and ^b Swedish Forest Products Research Laboratory, S-114 86 Stockholm, Sweden

A previous study¹ has shown that the action of sodium periodate on 2,4-dimethylphenol yields three products: 2,4-dimethyl-*p*-quinol, the Diels-Alder dimerization product² of 2,4-dimethyl-*o*-quinol, and the Diels-Alder adduct³ (1) of the *o*-quinol and 3,5-dimethyl-1,2-benzoquinone. We have now obtained from 2,4-dimethylphenol, in small yield, another periodate oxidation product, C₁₅H₁₈O₆, with m.p. $172.5-174.5^\circ\text{C}$. Crystallographic examination shows that it is 5,8-etheno-3,4a,7,9-tetramethyl-4a,5,6,7,8,8a-hexahydrochromene-7,8a-diol-2,6-dione (2), evidently formed by periodate oxidation of the adduct (1).



Experimental. The oxidation of 2,4-dimethylphenol with periodate was carried out and the oxidation mixture was worked up essentially as described in the previous paper.¹ From the acidification of 0.5 M aqueous NaOH solution with glacial acetic acid, a precipitate of a colourless compound, m.p. $172.5-174.5^\circ\text{C}$, was obtained. Its mass spectrum showed a molecular ion at m/e 278, calc. for C₁₅H₁₈O₆, 278.

X-Ray experimental and structure elucidation. Cell dimensions were determined, by least-squares refinement, from the angular positions of 25 well-centered reflexions on a Philips PW 1100 diffractometer. Crystal data are: $a = 16.513(4)$, $b = 6.987(2)$, $c = 12.146(4)$ Å, $\beta = 102.91(2)^\circ$, $V = 1366$ Å³, space group $P2_1/n$, $Z = 4$, $\rho_{\text{X-ray}} = 1.35$ g cm⁻³, $\mu(\text{CuK}\alpha) = 8.53$ cm⁻¹.

Only small single crystals were available. Data (set I) were collected using graphite monochromated CuK α radiation, $\theta-2\theta$ scan technique (scan width $1.5^\circ(\theta)$, scan rate $1^\circ(\theta)$ min⁻¹), and stationary background measurements at the ends of the scan interval. Of the

1909 unique reflexion intensities recorded out to $\theta = 58^\circ$, however, only 502 fulfilled the criterion that the net intensity, I , be greater than $2.5\sigma(I)$, where $\sigma(I)$ is based on counter statistics. Attempts to solve the structure by diverse direct method approaches failed, probably due to the difficulties of obtaining reliable triple-product sign relationships between different parts of the reflexion sphere. At this stage another crystal was used to collect a second data set (II). Of the 2570 unique reflexions collected out to $\theta = 70^\circ$, 1049 were considered significantly above background on the criterion $\sigma(I) < 0.3I$. All 20 non-hydrogen atoms were found from an E map computed with the best phase set obtained from the MULTAN⁴ direct phase determination procedure from 187 normalized $|E|$ values ≥ 1.8 (excluding the $|E|$ values greater than 4.3) and 1125 triple-product sign relationships.

With the exception of H(O16), which could not be positioned, the hydrogen atoms were located partly from chemical reasoning and partly from a difference Fourier synthesis. The positions, as well as assigned isotropic temperature factors, were included but not refined in the full-matrix least-squares treatment.

However, since the refinement of the structural parameters did not converge properly for set II, presumably as an effect of slight twinning in the crystal, set I was employed for the final refinement. Assuming anisotropic thermal parameters for the non-hydrogens, only half a molecule at a time could be refined with this set, due to the lack of data. The final value of R is 0.060. The Freeman⁵ scattering factors for C and O and those of Stewart *et al.*⁶ for H were used throughout the refinement, as well as the weighting scheme of Hughes.⁷ The final positional parameters for the non-hydrogen atoms are listed in Table 1, and those for the

Table 1. Positional parameters ($\times 10^4$) of the non-hydrogen atoms. Estimated standard deviations are given in parentheses.

ATOM	X	Y	Z
O(1)	3427(5)	7396(11)	5387(6)
C(2)	3930(7)	7464(22)	6436(11)
C(3)	4268(7)	5592(18)	7003(9)
C(4)	4068(8)	4044(17)	6445(9)
C(4A)	3522(8)	3737(17)	5321(10)
C(5)	2753(7)	2576(18)	5505(8)
C(6)	2194(8)	2181(18)	4343(11)
C(7)	1871(7)	4049(18)	3611(9)
C(8)	2237(8)	5669(18)	4406(10)
C(8A)	3191(7)	5695(19)	4727(8)
C(9)	1977(7)	5541(18)	5498(10)
C(10)	2213(7)	3866(17)	6049(9)
O(11)	4056(6)	9004(13)	6859(7)
C(12)	4796(8)	5836(25)	8150(10)
C(13)	3986(8)	2526(19)	4554(9)
O(14)	1943(6)	661(14)	3967(7)
C(15)	930(8)	4129(19)	3305(10)
O(16)	2161(5)	4014(13)	2606(5)
O(17)	3529(5)	5955(13)	3763(6)
C(18)	1442(8)	7025(18)	5889(9)

Table 2. Positional parameters ($\times 10^3$) of the hydrogen atoms.

ATOM	X	Y	Z
H(C4)	435	280	682
H(C5)	273	106	587
H(C8)	203	697	401
H(C10)	204	345	678
H1(C12)	495	444	876
H2(C12)	454	674	862
H3(C12)	536	633	813
H1(C13)	413	157	497
H2(C13)	354	215	383
H3(C13)	448	320	426
H1(C15)	80	560	289
H2(C15)	69	310	290
H3(C15)	84	401	402
H(O17)	309	672	320
H1(C18)	149	679	677
H2(C18)	89	704	521
H3(C18)	167	841	579

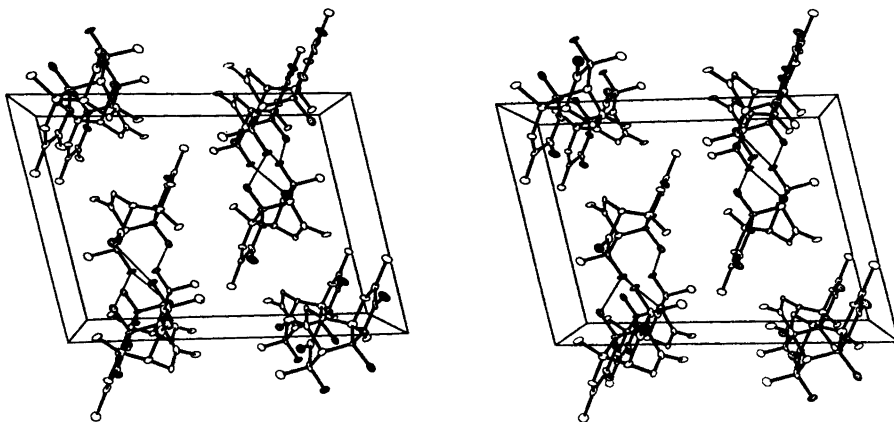


Fig. 1. A stereoscopic view of the molecular packing. Hydrogen atoms are omitted. Oxygens are marked with shaded ellipsoids. Intermolecular O—O contacts shorter than 3.0 Å are indicated as weak lines.

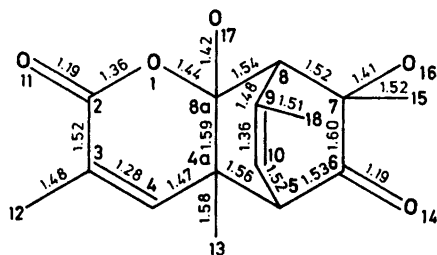


Fig. 2. Bond distances involving the non-hydrogen atoms.

hydrogens in Table 2. A list of the observed and calculated structure factors is available from the authors on request.

Results and discussion. The molecular geometry and packing pattern for this new type of periodate oxidation product from 2,4-dimethylphenol is shown in Fig. 1. Bond distances involving non-hydrogen atoms, as well as the numbering system used, are given in Fig. 2. The standard deviations of the bond distances are estimated to be in the range 0.012–0.018 Å; an effect of the lack of data. The derived C(3)–C(4) double bond length is 1.28 Å, which is more than 3σ shorter than what is generally observed. The C(sp^2)–C(sp^3) bond C(6)–C(7), on the other hand, is too long, perhaps indicating that the estimate of the esd's is too small. The C(4a)–C(8a) bond is lengthened, which is also observed in related compound,^{2,3,8–10} although the elongation measured in this investigation is not significant. The mean C–H bond length is 1.04 Å; the C–H bonds are distributed in the range 0.84–1.22 Å.

The O(1)–C(2)–C(3)–C(4)–C(4a)–C(8a) ring is planar within ± 0.018 Å, having the atoms C(4a) and C(8a) farthest out of the plane. The magnitudes of the torsion angles around this ring are less than 3.7° . The other three six-membered rings in the molecule are all boat-shaped.

Four short intermolecular O–O contacts are found between molecules related by the 2_1 axis at $\frac{1}{2}, y, \frac{1}{2}$ and its equivalents. These contacts are marked in Fig. 1 with weak lines. The atoms involved, their symmetry codes and the distances between them are:

$$\begin{aligned} \text{O}(14)^i - \text{O}(16)^{ii} &= 2.90 \text{ \AA} \quad (i \equiv x, y, z \\ ii &\equiv \frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z) \\ \text{O}(16)^i - \text{O}(17)^{ii} &= 2.79 \text{ \AA}. \end{aligned}$$

Only three other intermolecular contacts shorter than 3.5 Å are observed, neglecting the hydrogens:

$$\begin{aligned} \text{C}(5)^i - \text{O}(11)^{iii} &= 3.46 \text{ \AA} \quad (iii \equiv x, y - 1, z) \\ \text{O}(11)^i - \text{C}(15)^{iv} &= 3.45 \text{ \AA} \quad (iv \equiv x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}) \\ \text{O}(14)^i - \text{O}(17)^{ii} &= 3.24 \text{ \AA} \end{aligned}$$

This investigation has received financial support from the Swedish Natural Science Research Council and from the Tri-Centennial Fund of the Bank of Sweden. The authors are indebted to Professor Peder Kierkegaard for his stimulating interest in this investigation. We also wish to thank Dr. Sven Westman for correcting the English of this article.

1. Adler, E., Junghahn, L., Lindberg, U., Berggren, B. and Vestin, G. *Acta Chem. Scand.* **14** (1960) 1261.
2. Karlsson, B., Pilotti, A.-M. and Wiehager, A.-C. *Acta Chem. Scand.* **27** (1973) 2955.
3. Karlsson, B., Pilotti, A.-M. and Söderholm, A.-C. *Acta Chem. Scand. B* **31** (1977) 289.
4. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* **27** (1971) 368.
5. Freeman, A. J. *Acta Crystallogr.* **12** (1959) 261.
6. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
7. Hughes, E. W. *J. Am. Chem. Soc.* **63** (1941) 1737.
8. Karlsson, B., Pilotti, A.-M. and Wiehager, A.-C. *Acta Chem. Scand.* **27** (1973) 2945.
9. Karlsson, B., Pilotti, A.-M. and Wiehager, A.-C. *Acta Chem. Scand. B* **29** (1975) 411.
10. Karlsson, B., Pilotti, A.-M. and Wiehager, A.-C. *Acta Chem. Scand. B* **29** (1975) 1059.

Received March 22, 1977.