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Structure of 7-Hydroxy-2,8-dimethoxy-1,4-phenanthrenequinone

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Abstract. $C_{16}H_{12}O_5$, $M_r = 284\cdot28$, triclinic, $P\bar{1}$, $a = 7\cdot446$ (4), $b = 16\cdot921$ (14), $c = 10\cdot619$ (7) Å, $\alpha = 92\cdot18$ (6), $\beta = 107\cdot03$ (5), $\gamma = 95\cdot17$ (5)°, $V = 1271$ (2) Å^3, $Z = 4$, $D_x = 1\cdot485$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0\cdot7107$ Å, $\mu = 0\cdot120$ mm^{-1}, $F(000) = 592$, $T = 296$ K, $R = 0\cdot065$ for 1917 observed reflections. The asymmetric unit contains two molecules, giving rise to pseudosymmetry and superstructure phenomena. The molecules consist of aromatic rings of different planarity. The aromatic skeletons are inclined at 8 (1)° to each other. Neighbouring molecules are connected *via* hydrogen bonds along |101|. Weak C—H···O interactions contribute to structural stability.

Introduction. The title compound, named cypripedin, is a naturally occurring quinone isolated from *Cypripedium calceolus* L. Cypripedin and other quinones from *Cypripedium* species are known to cause allergic skin reactions (Hausen, 1982). In the course of investigations on structure–function relationships of allergenic constituents of plants and plant materials (Schmalle, Jarchow, Hausen & Schulz, 1983), the

structure of cypripedin was determined. Owing to the small quantity of separated substance no chemical formula or mass spectrometric data was available when starting the X-ray investigation.

Experimental. Title compound separated and concentrated by repetitive thin-layer chromatography, dark red crystals recrystallized from solution of acetone and benzene (40/60) ($v/v = 1:1$); crystal dimensions $0\cdot2 \times 0\cdot6 \times 0\cdot7$ mm; space-group determination from Weissenberg photographs; Syntex $P2_1$ diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; cell dimensions from least-squares refinement of 14 reflections within shell $5 \le 2\theta \le 25°$; $(\sin\theta/\lambda)_{max} = 0\cdot527$ Å^{-1}; $\theta/2\theta$ scan mode, variable scan speed from $1\cdot0$ to $29\cdot3°$ min^{-1}; $0 \le h \le 6$, $-17 \le k \le 17$, $-11 \le l \le 11$; loss in intensity of standard reflections 143 and 025 less than 1%, monitored at the beginning and after every 98 reflections (32 times) during data collection; 3104 reflections measured, Lorentz–polarization, no absorption correction; 3040 unique reflections, 1917 with $I > 1\cdot96\sigma(I)$, 1123 unobserved; structure solved by direct methods (Bartsch, Jarchow & Schmalle, 1980), anisotropic full-matrix least-squares refinement based on $F(hkl)$; all H-atom positions from difference Fourier syntheses, not refined; isotropic

temperature parameters on H atoms calculated before last two cycles of refinement as B_{eq} from thermal parameters of atoms to which they are bonded; final refinement (379 parameters) with positional parameters and anisotropic temperature factors for C and O atoms varied, $wR(R) = 0.041$ (0.065), $w = 1/\sigma^2(F)$; max. shift/e.s.d. $= 0.28$ on positional and 0.45 on thermal parameters; max. and min. heights in final difference Fourier synthesis 0.28 and -0.32 e Å^{-3}; computer programs used: MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), SHELX76 (Sheldrick, 1976), ORXFLS (Busing, Martin, Levy, Ellison, Hamilton, Ibers, Johnson & Thiessen, 1971), ORFFE (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1971), ORTEP (Johnson, 1966); neutral atomic scattering factors from International Tables for X-ray Crystallography (1974).

Discussion. The final atomic parameters are given in Table 1.* The asymmetric unit contains two molecules of the same chemical composition. As can be seen from Fig. 1, part of the structure contains a pseudo-translation of $b/2$. Sixteen pairs, e.g. C(15')–O(5), O(3')–C(8), C(2')–C(14) etc., were detected and found to have minor differences in the x and z positional parameters, but vary by nearly 0.50 in the y positional parameters. Although a twofold pseudoaxis transforms the two molecules into each other, the deviations from this symmetry are significant. The pseudoplanarity of the asymmetric unit creates centers of pseudosymmetry, one of which is indicated in Fig. 1. The resulting difficulties for structure determinations were solved (Bartsch et al., 1980) by combining the negative-quartet procedure of the SHELX system with MULTAN.

Bond distances and angles are shown in Fig. 2. With the exception of O(3)–C(15) = 1.444 (8), O(3')–C(15') = 1.478 (8) and C(8)–C(14) = 1.399 (9), C(8')–C(14') = 1.423 (9) Å, all comparable bond lengths of the two molecules are equivalent within 1σ. Differences in bond angles were found for O(4)–C(7)–C(8) = 117.0 (6), O(4')–C(7')–C(8°) = 122.3 (5); O(4)–C(7)–C(6) = 121.8 (5), O(4')–C(7')–C(6') = 118.7 (6); C(5)–C(6)–C(7) = 120.2 (5), C(5')–C(6')–C(7') = 123.4 (5)°. The most pronounced deviations of the adjacent molecules are shown in selected dihedral angles, which are given in Table 2.

Double bonds between atomic positions 2–3, 9–10, 11–12 and in the keto groups of the quinone rings are well established. Bonds of the phenanthrene rings C and

D (Fig. 2) have no uniform character. Distances between positions 5–6 and 7–8 are considerably shortened to values between 1.369 and 1.381 Å, whereas bonds are lengthened to 1.423 to 1.434 Å at the positions 5–13 and 13–14. Similar deviations were found in the structure of phenanthrene (Kay, Okaya & Cox, 1971).

Table 1. *Final atomic coordinates* ($\times 10^4$) *and* U_{eq} *of* 7-hydroxy-2,8-dimethoxy-1,4-phenanthrenequinone *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}(Å^2)*
O(1)	4431 (7)	9101 (3)	2075 (4)	0.058
O(2)	8715 (7)	11255 (2)	5726 (4)	0.061
O(3)	4482 (6)	10587 (2)	1485 (4)	0.046
O(4)	11296 (6)	8657 (2)	10046 (4)	0.048
O(5)	8904 (6)	7682 (2)	8048 (4)	0.046
C(1)	5431 (9)	9588 (4)	2923 (6)	0.042
C(2)	5559 (9)	10445 (4)	2697 (6)	0.036
C(3)	6659 (9)	10969 (4)	3631 (6)	0.041
C(4)	7753 (9)	10731 (4)	4915 (6)	0.039
C(5)	9930 (9)	10092 (3)	7523 (6)	0.038
C(6)	10832 (9)	9783 (4)	8695 (6)	0.037
C(7)	10506 (9)	8979 (4)	8862 (6)	0.041
C(8)	9334 (9)	8471 (4)	7857 (6)	0.036
C(9)	7226 (9)	8243 (3)	5606 (6)	0.041
C(10)	6337 (9)	8521 (4)	4430 (6)	0.041
C(11)	6522 (9)	9338 (4)	4221 (6)	0.034
C(12)	7678 (9)	9882 (3)	5216 (6)	0.030
C(13)	8665 (9)	9595 (4)	6458 (6)	0.031
C(14)	8430 (8)	8769 (4)	6649 (6)	0.031
C(15)	4577 (9)	11399 (4)	1117 (6)	0.059
C(16)	10380 (10)	7198 (4)	8121 (7)	0.066
O(1')	9955 (6)	5063 (2)	7353 (4)	0.047
O(2')	6110 (6)	2988 (2)	3407 (4)	0.058
O(3')	9812 (6)	3548 (2)	7822 (4)	0.048
O(4')	2034 (6)	5714 (3)	222 (4)	0.058
O(5')	4392 (6)	6659 (2)	1882 (4)	0.051
C(1')	8946 (9)	4597 (4)	6467 (6)	0.036
C(2')	8796 (9)	3721 (4)	6609 (6)	0.042
C(3')	7807 (9)	3214 (4)	5606 (6)	0.042
C(4')	6787 (9)	3493 (4)	4319 (6)	0.040
C(5')	4214 (9)	4181 (3)	1938 (6)	0.039
C(6')	3122 (9)	4545 (4)	882 (6)	0.047
C(7')	3177 (9)	5366 (4)	818 (6)	0.045
C(8')	4377 (9)	5845 (4)	1843 (6)	0.042
C(9')	6770 (9)	6020 (3)	4010 (6)	0.039
C(10')	7837 (9)	5712 (4)	5119 (6)	0.038
C(11')	7777 (9)	4880 (4)	5218 (6)	0.033
C(12')	6664 (8)	4363 (4)	4175 (6)	0.031
C(13')	5479 (9)	4665 (4)	3026 (6)	0.034
C(14')	5547 (9)	5512 (4)	2963 (6)	0.032
C(15')	9634 (9)	2701 (4)	8106 (6)	0.062
C(16')	5160 (10)	7047 (4)	959 (7)	0.072

$$ * \; U_{eq} = (6\pi^2)^{-1} \sum_{i,k} \beta_{ik}(\mathbf{a}_i \cdot \mathbf{a}_k). $$
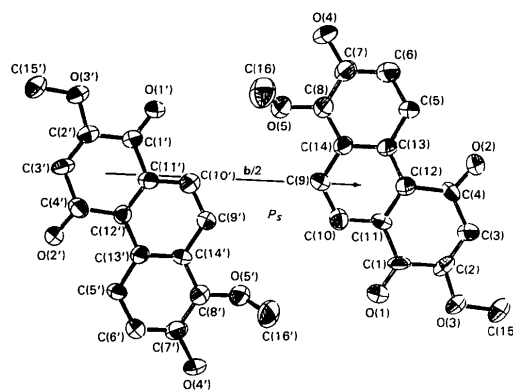

Fig. 1. Perspective view of cypripedin with atom numbering. The thermal ellipsoids are drawn at the 50% probability level. Elements of pseudosymmetry are indicated.

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* List of structure factors, anisotropic thermal parameters and positional H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42553 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ring systems B to F are planar or nearly planar with maximum deviations occurring in ring B. Ring A is distorted with largest distances from the mean plane of 0·059 (7) Å at C(4′) and 0·047 (7) Å at C(1′) and C(12′). These distortions are mainly caused by O(1′) and O(2′), which are out of the plane by 0·123 (5) and 0·237 (5) Å, respectively. Calculation of the mean planes for the carbon skeleton of the discrete molecules revealed an inclination of 8 (1)°. Of the two methoxy groups of each molecule in the title compound, one is nearly planar with dihedral angles C(15)—O(3)—C(2)—C(3) = 3 (1) and C(15′)—O(3′)—C(2′)—C(3′) = −7 (1)°. The angles for the other methoxy substituents are: C(16)—O(5)—C(8)—C(7) = −75 (1) and C(16′)—O(5′)—C(8′)—C(7′) = −71 (1)°. If, for example, C(16) was in the plane, then steric hindrance from H atoms at O(4) and C(9) would appear.

The crystal packing is shown in Fig. 3. Planes of molecules are approximately parallel to (10$\bar{1}$). Within each sheet molecules are connected via hydrogen bonds. The distances O(1)···O(4) = 2·696 (5), O(1′)···O(4′) = 2·717 (5), O(4)—H(4) = 0·87, O(4′)—H(4′) = 0·85, O(1)···H(4) = 1·98 and O(1′)···H(4′) = 1·95 Å and the angles at H(4) and H(4′), 139 and 148° respectively, confirm strong hydrogen bonds (Kuleshova & Zorkii, 1981). Short intermolecular
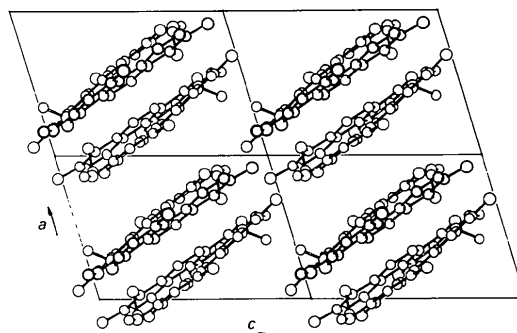

Fig. 3. Projection of four unit cells on (101). H atoms are omitted for clarity.

C···O contacts (Sutor, 1963) are assumed to contribute to the dense packing of the molecules. Four such contacts with C···O distances less than 3·6 Å and O···H less than 2·6 Å have consistent angles at the hydrogens. For the shortest values, O(5′)···C(15′) [1 − x, 1 − y, 1 − z] = 3·28 (1), O(5′)···H(151′) = 2·52 Å, the angle is O(5′)···H(151′)—C(15′) = 135°.

Fig. 2. Bond lengths (Å) and angles (°) for cypripedin. E.s.d.s for bond lengths are 0·007–0·010 Å, and for angles 0·5–0·6°. For atom numbering see Fig. 1.

Table 2. Selected torsion angles (°)

E.s.d.'s are about 1°.

Molecule A		Molecule B	
C(15) O(3) C(2) C(3)	3	C(15′)—O(3′)—C(2′)—C(3′)	−7
O(2) C(4) C(12) C(13)	1	O(2′)—C(4′)—C(12′)—C(13′)	11
C(3) C(4) C(12) C(11)	0	C(3′)- C(4′)—C(12′)—C(11′)	10
O(2) C(4) C(12) C(11)	179	O(2′)—C(4′)—C(12′)—C(11′)	−169

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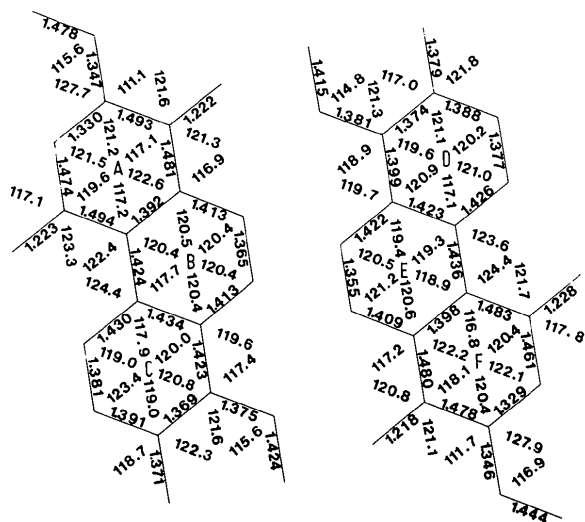SUTOR, D. J. (1963). J. Chem. Soc. pp. 1105–1110.