0.95 and methyl C—H = 0.98 Å. As the structure contains only C, H, N and O atoms, and due to the kind of radiation used, the absolute structure could not be determined.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

I thank Dr G. Schütz, University of Frankfurt, for providing the sample.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1146). Services for accessing these data are described at the back of the journal.

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7-Methoxy-2,2-dimethyl-3-phenyl-4-(4-hydroxyphenyl)-2*H*-1-benzopyran†

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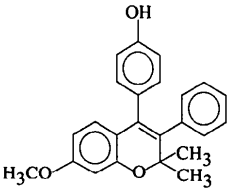
Abstract

The crystal structure of the title compound, $C_{24}H_{22}O_3$, shows that both the pendant phenyl substituents at C3 and C4 have a twist conformation, while the pyran ring adopts a distorted sofa conformation due to puckering at C2 by the dimethyl substitutions.

† CDRI Communication No. 5662.

Comment

In the course of our ongoing work on the synthesis and structure–activity relationship studies of a series of non-steroidal antiestrogens, the title compound, (I), which elicited an estrogenic response, was synthesized (Ray *et al.*, 1976). A closely related compound, centchroman, was found to be associated with potent estrogen antagonistic activity along with weak estrogenic activity (Kamboj *et al.*, 1977). Since both estrogen agonist and antagonist activities are mediated through the estrogen receptor, it was of interest to study the spatial differences in the molecular structures of the two compounds which would account for this differential behaviour. Recently, the X-ray structures of both the racemate and *d*-enantiomer of centchroman (as the *N*-methyl iodide salt) have been reported in order to explore their configuration–activity relationships (Ray *et al.*, 1994; Srivastava *et al.*, 1996). In this communication, we report the X-ray single-crystal structure determination of the title compound and use molecular graphics to compare it's structure with both the *dl*-centchroman methyl iodide salt and estradiol.



(I)

The conformation of the title molecule along with the atom-numbering scheme is shown in Fig. 1. The molecule contains one fused-ring system (*A*/*B*) and two phenyl rings (*C* and *D*). All three aromatic rings, *A*, *C* and *D*, are planar [deviations of the atoms from their least-squares planes are within the range −0.018 (1)–0.025 (1) Å], while ring *B* is puckered. In ring *B*, atoms C2 and O25 deviate by 0.423 (3) and −0.216 (3) Å, respectively, from the least-squares plane through C3, C4, C5 and C1, which indicates that the ring has a tendency to adopt a sofa conformation. Both the 3- and 4-substituted pendant phenyl rings showed a tendency to be perpendicular with respect to the plane through the *A*/*B* chromene ring (the dihedral angles between the planes *A*/*B* and *C* is 99.4°, and between *A*/*B* and *D* is 109.4°) as has been found in the centchroman structure (Ray *et al.*, 1994). Fig. 2 shows that the molecules are connected by intermolecular hydrogen bonding [O27—H···O25 2.848 (2) Å], thus, the crystal structure is stabilized mainly by hydrogen-bonding and van der Waals interactions.

It has been speculated (Durani *et al.*, 1979) that estrogen antagonists, which act through competitive inhibition of estradiol action, carry a substructural entity in their molecular framework which simulates estradiol and is responsible for its binding to the receptor.

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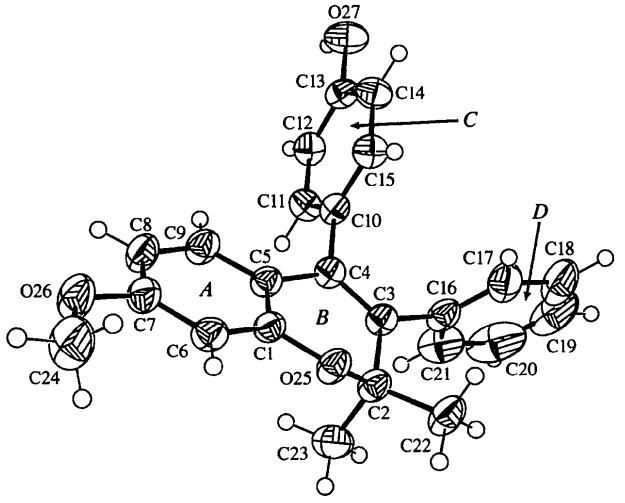

Fig. 1. *ORTEP* (Johnson, 1965) diagram showing displacement ellipsoids at 50% probability for the non-H atoms.

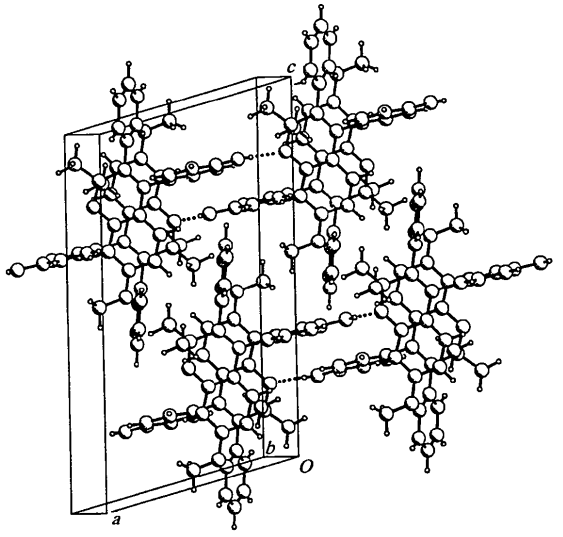

Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) crystal-packing diagram showing the hydrogen bonds as dotted lines.

However, an additional binding unit attached to these molecules somehow interferes with the initiation of the estrogenic response. An overlay of the title molecule with the centchroman (Ray *et al.*, 1994) and *d*-estradiol (Busetta *et al.*, 1972) is shown in Fig. 3. This structural comparison clearly shows that there is significant overlap when the phenyl residue of benzopyran is made to coincide with the aromatic moiety of estradiol having its 7-methoxy group occupying the position of the phenolic hydroxyl group and the 3-phenyl unit projecting in the area of the *D* ring of estradiol; when overlapped with centchroman, the area of the pyrrolidine substituent in centchroman remains unoccupied. This is in accordance with our earlier proposed estrogen receptor model (Durani *et al.*, 1979) which demands that a segment of the molecule in the region be occupied by the pyrrolidine moiety (denoted as region *E*) for estrogen antagonist activity. Absence of this unit in the title compound is possibly responsible for the lack of antagonist activity.

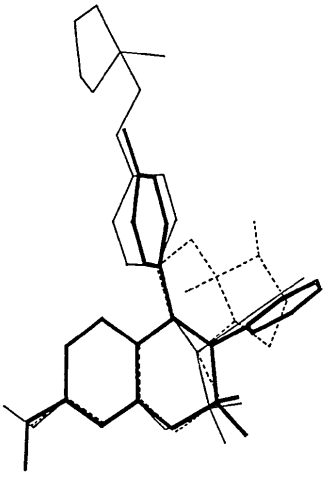

Fig. 3. Superposition of the title molecule (bold lines) with centchroman (thin lines) and estradiol (broken lines). Superposition was achieved by fitting three atoms of the aromatic ring in the fused-ring system (*ALCHEMY*-III; Tripos Associates Inc., 1972).

Experimental

The synthesis of compound (I) was performed by reacting 3-phenyl-4-(4-hydroxyphenyl)-7-methoxycoumarin with methyl magnesium iodide in dry ether according to a procedure described previously (Ray *et al.*, 1976). Diffraction quality crystals were obtained by slow evaporation from methanol solution at room temperature.

Crystal data

$C_{24}H_{22}O_3$
M_r = 358.42
Monoclinic
$P2_1/n$
a = 10.236 (2) Å
b = 10.258 (2) Å
c = 18.827 (4) Å
β = 105.10 (2)°
V = 1908.6 (7) Å^3
Z = 4
D_x = 1.247 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 30–45°
μ = 0.646 mm^{-1}
T = 293 (2) K
Block
0.35 × 0.25 × 0.20 mm
Colourless

Data collection

Siemens *R3/m* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2740 measured reflections
2573 independent reflections
2266 reflections with $I > 2\sigma(I)$
R_{int} = 0.011

θ_{max} = 57.06°
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 0$
$l = -20 \rightarrow 19$
3 standard reflections every 97 reflections
intensity decay: <5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.102$
$S = 1.071$
2570 reflections
245 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.4791P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.181$ e Å^{-3}
$\Delta\rho_{min} = -0.185$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0178 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

The structure was solved by direct methods and refined anisotropically on non-H atoms by using full-matrix least-squares methods. All H atoms were placed in idealized positions geometrically and allowed to ride with the parent atom to which each was bonded for the final cycles of refinement. Three reflections $[\Delta(F^2)/\sigma > 5.0]$ were suppressed during the last cycles of refinement.

Data collection: Siemens *P*3 software. Cell refinement: Siemens *P*3 software. Data reduction: Siemens *P*3 software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965), *PLUTO* (Motherwell & Clegg, 1978) and *ALCHEMY*-III (Tripos Associates Inc., 1972). Software used to prepare material for publication: *CIFTAB SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1041). Services for accessing these data are described at the back of the journal.

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5-Amino-1-phenylsulfonyl-4-pyrazolin-3-one

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Abstract

The title compound, $C_9H_9N_3O_3S$, crystallizes with two independent molecules in $P2_1$, although the symmetry is close to $P2_1/c$. The keto tautomer is the only solid-state form. The main difference between the two molecules is the orientation of the phenyl rings. The five-membered rings are planar. An extensive hydrogen-bonding system connects the molecules into layers parallel to the *xy* plane.

Comment

We are interested in the synthesis and properties of antimetabolites (Elgemeie, Attia *et al.*, 1994; Elgemeie & Hussain, 1994; Elgemeie, El-Ezbawy *et al.*, 1994) and have extensively investigated the synthesis of *N*-sulfonated heterocycles. We report here the synthesis and structure of the *N*-sulfonated pyrazole (3), obtained by intramolecular cyclization of cyanoaceto-*N*-phenylsulfonylhydrazide, (1).