C2—C3	1.518 (2)	N8—C9	1.461 (2)
C3—N4	1.456 (2)	C9—C10	1.512 (2)
N4—C5	1.333 (2)	C10—N11	1.462 (2)
C5—O5	1.219 (1)	N11—C12	1.463 (2)
C5—C6	1.538 (2)	C12—C13	1.520 (2)
C2—N1—C13	115.1 (1)	O7—C7—N8	125.9 (1)
N1—C2—C3	110.8 (1)	O7—C7—C6	119.3 (1)
N4—C3—C2	111.8 (1)	N8—C7—C6	114.6 (1)
C5—N4—C3	123.4 (1)	C7—N8—C9	123.4 (1)
O5—C5—N4	125.7 (1)	N8—C9—C10	111.4 (1)
O5—C5—C6	120.4 (1)	N11—C10—C9	109.3 (1)
N4—C5—C6	113.82 (9)	C10—N11—C12	115.8 (1)
N6—C6—C7	109.3 (1)	N11—C12—C13	108.7 (1)
N6—C6—C5	109.58 (8)	N1—C13—C12	110.1 (1)
C7—C6—C5	107.0 (1)		
C3—N4—C5—O5	6.1 (2)	C6—C7—N8—C9	169.0 (1)
C3—N4—C5—C6	−170.7 (2)	O7—C7—N8—C9	−6.7 (2)

Data collection: *CAD-4F Software* (Enraf–Nonius, 1989). Data reduction: *Xtal* (Hall, King & Stewart, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *Xtal*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *Xtal*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1095). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 3102–3104

A Corticosteroid Ester

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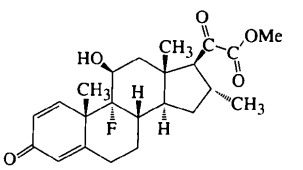
Abstract

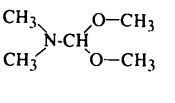
The unit cell of the title compound, 9α-fluoro-11β-hydroxy-21-methoxy-16α-methylpregna-1,4-diene-3,20,-21-trione, $C_{23}H_{29}FO_5$, contains two symmetry-related molecules and no solvent. One of the five O atoms is hydrogen-bonded to a neighbouring molecule.

Comment

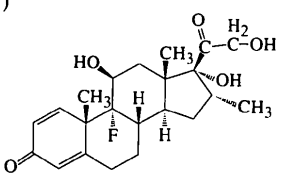
The title compound, (1), belongs to a family of corticosteroid esters possessing high topical anti-inflammatory activity without any systemic effects. Their synthesis has already been described (Laurent, Gerhards & Wiechert, 1975), but a new synthetic route by reaction of *N,N*-dimethylformamide dimethyl acetal (DMF-DMA), (2), on artificial corticosteroid dexamethasone, (3), has recently been established. This latter DMF-DMA reaction represents a far simpler way of synthesizing corticosteroid esters. The structure of the major reaction product, (1), has been determined with high-resolution mass spectrometry and nuclear magnetic resonance (Negriolli, Maume, Deniaud & André, 1996). However, in order to confirm the results and analyse the packing of the molecules, an X-ray structure determination was carried out.



(1)



(2)



(3)

An *ORTEP* (Johnson, 1965) plot of (1) is shown in Fig. 1. This molecule is based upon the cyclo-

pentanoperhydrophenanthrene nucleus. The double bond between C1 and C2 is characteristic of artificial corticosteroid structures (natural corticosteroids such as cortisone do not have this double bond). The bond distances are in good agreement with literature values (Allen *et al.*, 1987). The unit cell contains two symmetry-related molecules. The carbonyl-O atom O1 is hydrogen-bonded to the O2—H16 hydroxyl group of a molecule related by a 2_1 screw-axis [O1···H16 2.13 (4) Å], linking the molecules in chains and thereby strengthening the three-dimensional arrangement.

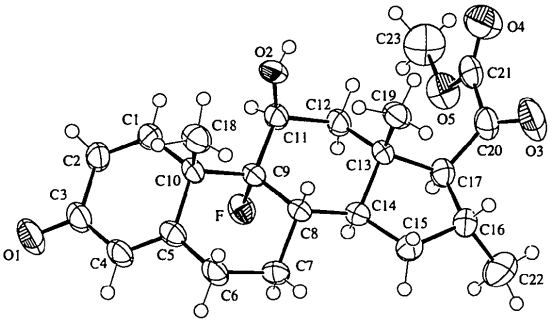


Fig. 1. *ORTEP* (Johnson, 1965) view of $C_{23}H_{29}O_5F$. Displacement ellipsoids are shown at the 50% probability level. The H-atom displacement parameters have been set arbitrarily small for clarity.

Experimental

The title compound was prepared as reported by Negriolli *et al.* (1996). X-ray quality crystals were obtained by slow crystallization from acetonitrile at 300 K.

Crystal data

$C_{23}H_{29}FO_5$
M_r = 404.48
Monoclinic
$P2_1$
a = 7.7176 (16) Å
b = 17.328 (4) Å
c = 7.8162 (15) Å
β = 93.620 (16)°
V = 1043.2 (4) Å^3
Z = 2
D_x = 1.288 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–20°
μ = 0.10 mm^{-1}
T = 293 K
Plate
0.76 × 0.55 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4F diffractometer
ω scans
Absorption correction: analytical
T_{min} = 0.96, T_{max} = 0.99
9688 measured reflections
9168 independent reflections
5707 observed reflections [$F > 4\sigma(F)$]

R_{int} = 0.029
θ_{max} = 34.95°
$h = -12 \rightarrow 12$
$k = -27 \rightarrow 27$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: negligible

Refinement

Refinement on F
R = 0.059
wR = 0.059
S = 1.421
4637 reflections
366 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.02F_o^2)]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Extinction correction: Zachariasen (1968)
Extinction coefficient: 0.003 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
F	0.1223 (2)	0.82240	0.2142 (2)	0.0413 (8)
O1	−0.2146 (3)	0.62750 (14)	0.4893 (3)	0.0629 (13)
O2	0.2143 (3)	0.96405 (15)	0.5353 (3)	0.0524 (12)
O3	0.6798 (3)	1.12275 (16)	0.0508 (4)	0.0807 (17)
O4	0.3908 (3)	1.20371 (17)	0.1484 (4)	0.0728 (16)
O5	0.2486 (3)	1.12273 (16)	−0.0322 (3)	0.0579 (13)
C1	−0.0197 (4)	0.81168 (17)	0.5429 (4)	0.0393 (14)
C2	−0.1399 (4)	0.75728 (18)	0.5407 (4)	0.0453 (15)
C3	−0.1013 (4)	0.67739 (17)	0.4963 (4)	0.0443 (15)
C4	0.0773 (4)	0.66051 (16)	0.4601 (4)	0.0417 (14)
C5	0.2011 (3)	0.71443 (16)	0.4622 (3)	0.0367 (13)
C6	0.3821 (4)	0.69663 (17)	0.4182 (4)	0.0427 (14)
C7	0.4431 (4)	0.75072 (16)	0.2807 (4)	0.0403 (14)
C8	0.4143 (3)	0.83605 (15)	0.3222 (3)	0.0308 (12)
C9	0.2237 (3)	0.84968 (15)	0.3603 (3)	0.0308 (12)
C10	0.1663 (3)	0.79754 (16)	0.5116 (3)	0.0345 (12)
C11	0.1674 (4)	0.93488 (16)	0.3694 (4)	0.0371 (13)
C12	0.2402 (4)	0.98444 (17)	0.2252 (4)	0.0385 (14)
C13	0.4334 (3)	0.97358 (15)	0.2079 (3)	0.0320 (12)
C14	0.4635 (3)	0.88717 (16)	0.1740 (3)	0.0332 (12)
C15	0.6475 (4)	0.8826 (2)	0.1144 (4)	0.0458 (16)
C16	0.6750 (4)	0.9593 (2)	0.0193 (4)	0.0429 (14)
C17	0.5088 (3)	1.00661 (17)	0.0416 (3)	0.0370 (13)
C18	0.2711 (5)	0.8128 (2)	0.6845 (4)	0.0475 (16)
C19	0.5431 (4)	1.00407 (19)	0.3640 (4)	0.0433 (15)
C20	0.5406 (4)	1.09278 (19)	0.0481 (4)	0.0459 (15)
C21	0.3847 (4)	1.14710 (19)	0.0627 (4)	0.0466 (16)
C22	0.7140 (7)	0.9485 (3)	−0.1665 (5)	0.078 (3)
C23	0.0920 (6)	1.1695 (3)	−0.0209 (7)	0.079 (3)

All H atoms were found through difference Fourier syntheses and those of the CH_2 and CH_3 groups were refined with constrained isotropic displacement parameters; others were refined freely and isotropically.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal* (Hall, King & Stewart, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *Xtal*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *Xtal*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 3104–3105

(*E*)-3-(4-Chlorophenyl)-3-cyclopropyl-2-(phenylthio)acrylonitrile

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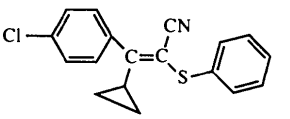
Abstract

The unambiguous identification of the *E* configuration of the title compound, $C_{18}H_{14}ClNS$, confirms a previous tentative assignment from NMR spectroscopic data. Bond lengths and angles are normal. The plane containing the acrylyl group makes angles of 98.0 (1) and 87.6 (3)° with the planes of the *p*-chlorophenyl and cyclopropyl rings, respectively, preventing conjugation.

Comment

The versatility of vinyl sulfides makes them highly valued synthetic intermediates. In addition, certain unsaturated sulfides, particularly vinyl sulfides, have been found to have significant negative inotropic activities (Gautier, Roche, Métin, Carpy & Madesclaire, 1995) and have also displayed useful biological activities as pesticides, bactericides (Erhardt, Ertel, Mildenberger, Sachse & Hartz, 1979) and oxygen-radical scavengers (Duroux, Roche & Madesclaire, 1991). Knowledge of the exact configuration of the *Z* and *E* diastereoisomers was required to conduct a pharmacological study and establish structure–activity relationships. Also, these readily accessible *gem*-functionalized vinyl sulfides are useful intermediates in the synthesis of sulfonamides, which are of great interest in cardiovascular pharmacology.

We report here the X-ray crystal structure determination of the title compound, (1). The results confirm the *E* configuration of this diastereoisomer, as already suggested by NMR spectroscopic data (Roche & Madesclaire, 1996).



(1)

Bond lengths and angles are consistent with previous results. In particular, values for S—C bond lengths [S(13)—C(2) 1.766 (4) and S(13)—C(14) 1.769 (3) Å] and C=C—S and C—S—C angles [C(3)=C(2)—S(13) 123.6 (3) and C(2)—S(13)—C(14) 103.7 (2)°] are consistent with published values for other vinyl sulfides; respective corresponding values are 1.752 (10) and 1.794 (12) Å, and 127.0 (2) and 102.5 (2)° (Derissen & Bijen, 1973), 1.759 (8) and 1.795 (8) Å, and 127.5 (7) and 102.1 (5)° (Samdal, Seip & Torgrimsen, 1979), 1.752 (2) and 1.793 (3) Å, and 124.9 (2) and 100.1 (1)° (Métin, Roche, Veschambre & Madesclaire, 1992), and 1.755 (2) and 1.768 (2) Å, and 123.2 (1) and 103.0 (1)° (Gautier *et al.*, 1995).

The length of the C≡N triple bond [1.143 (5) Å] is in the normal range [1.133 (6)–1.152 (7) Å; Rabinovich & Shakked, 1978]. Also, the length of the C(1)—C(2) bond [1.438 (5) Å] shows it to be a single σ bond, excluding any π delocalization between the vinyl C(2)=C(3) double bond and the nitrile C(1)≡N(20) triple bond.

The central C(2)=C(3) vinyl group and atoms S(13), C(1), C(4) and C(10) are nearly coplanar, the maximum deviation from the best plane being 0.070 (4) Å. As expected, the N(20) atom lies in this plane, with a deviation of 0.024 (4) Å.

The plane defined by the vinyl group forms an angle of 98.0 (1)° with the plane of the *p*-chlorophenyl ring, which prevents π-electron conjugation, and an angle of 87.6 (3)° with the cyclopropane ring.

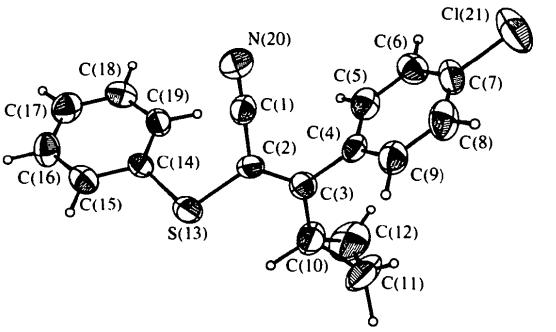


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the title compound showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels.