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3-Methoxy-1′-phenyl-4′*β*,5-dihydro-1*H*-pyrazolo[4′,3′:16,17]estra-1,3,5(10)-triene

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The regio- and stereochemistry of the title compound, $C_{26}H_{30}N_2O$, has been established by X-ray analysis. The configuration of the stereogenic centre at C-16 proved to be *S* and the H atom at C-16 adopts the *β* position.

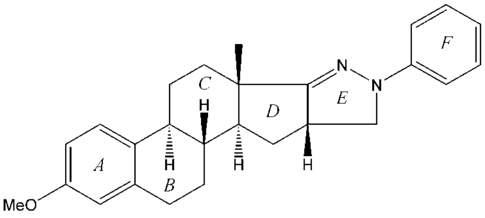
Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.092
Data-to-parameter ratio = 7.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The synthesis of the title compound, (I), *via* a boron trifluoride diethyl etherate-induced 1,3-dipolar cycloaddition of the intermediate phenylhydrazone derived from the corresponding D-secoestrone aldehyde, will be published elsewhere (Frank *et al.*, 2002). The product has a newly formed stereogenic centre at the C-16 position, and the assignment of the stereochemistry at this position was the reason for the present study.



(I)

The structural study has shown that the H atom at the C-16 adopts the *β* position (Fig. 1). The *B*/*C* and *C*/*D* ring junctions are all-*trans*. Ring *A* is planar, ring *B* adopts a distorted half-chair conformation, and ring *C* displays a chair conformation. The *D* and *E* rings have envelope conformations, with atoms C13 and C16*A* displaced by 0.651 (4) and 0.436 (4) Å, respectively, from the planes of the remaining atoms of the corresponding rings.

For the crystal structures of some other related estrone derivatives, see Bes *et al.* (1997, 1998), Noltemeyer *et al.* (1996), Hooft & Kroon (1995), van Geerestein *et al.* (1987) and Duax *et al.* (1991).

Experimental

For the synthesis of the title compound, (I), 16,17-seco-3-methoxy-estra-1,3,5(10)16-tetraen-17-al (298 mg, 1.00 mmol), phenylhydrazine (0.10 ml, 109 mg) and 2 drops of glacial acetic acid were reacted in ethanol (10 ml). The mixture was stirred for 2 h at room temperature. The resulting phenylhydrazone derivative (369 mg, 95%), when treated (after purification) with a catalytic amount of 48% $BF_3 \cdot OEt_2$ (0.07 ml, 0.25 mmol) in ice-cold CH_2Cl_2 (5 ml), undergoes intramolecular cyclization to afford (I) as a main product (290 mg, 79%). After purification by column chromatography (CH_2Cl_2) on silica gel, the product was crystallized from a 1:1 mixture of CH_2Cl_2/light petroleum at 298 K (m.p. 451–453 K). Spectroscopic analysis, ^{1}H

NMR ($CDCl_3$, δ, p.p.m.): 1.10 (*s*, 3H, $18H_3$), 2.84 (*m*, 2H, $6H_2$), 2.96 (*dd*, 1H, J = 13.3 Hz, J = 10.5 Hz, 16$a\beta$–H), 3.36 (*m*, 1H, 16H), 3.77 (*s*, 3H, 3–OMe), 4.20 (*dd*, 1H, J = 10.5 Hz, J = 9.6 Hz, 16$a\alpha$–H), 6.63 (*d*, 1H, J = 2.4 Hz, 4H), 6.72 (*dd*, J = 8.6 Hz, J = 2.4 Hz, 2H), 6.84 (*t*, 1H, J = 7.4 Hz, 4′–H), 7.07 (*d*, 2H, J = 8.2 Hz, 2′–H and 6′–H), 7.23 (*m*, 3H, 1H, 3′–H and 5′–H); ^{13}C NMR ($CDCl_3$, δ, p.p.m): 14.7 (C-18), 25.9, 26.7, 26.8, 29.6, 32.9, 38.6, 40.8, 44.2, 45.0, 54.8 (C-16), 55.2 (3–OMe), 58.4 (C-16*a*), 111.5 (C-2), 113.9 (3C, C-4, C-2′ and C-6′), 119.3 (C-4′), 126.3 (C-1), 128.9 (2C, C-3′ and C-5′), 132.1 (C-10), 137.6 (C-5), 148.9 (C-1′), 157.6 (C-3), 172.1 (C-17); analysis calculated for $C_{26}H_{30}N_2O$: C 80.79, H 7.82, N 7.25%; found: C 80.62, H 7.96, N 7.45%.

Crystal data

$C_{26}H_{30}N_2O$
M_r = 386.52
Orthorhombic, $P2_12_12_1$
a = 6.120 (1) Å
b = 8.950 (1) Å
c = 37.622 (4) Å
V = 2060.7 (5) Å^3
Z = 4
D_x = 1.246 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3250 reflections
θ = 2.2–24.7°
μ = 0.08 mm^{-1}
T = 133 (2) K
Block, colourless
0.3 × 0.2 × 0.2 mm

Data collection

Locally modified Stoe–Siemens–Huber four-circle diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.978, T_{max} = 0.985
23229 measured reflections

1939 independent reflections
1669 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 24.7°
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 43$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.092
S = 1.09
1939 reflections
264 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 0.5351P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Friedel pairs were merged, because of the lack of significant anomalous scattering. H atoms were included in calculated positions and refined using a riding model. The U_{eq} values of the H atoms were set to 1.5 times the U_{eq} values of the attached atom for methyl groups and 1.2 times the U_{eq} values of the attached atom for all the remaining H atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

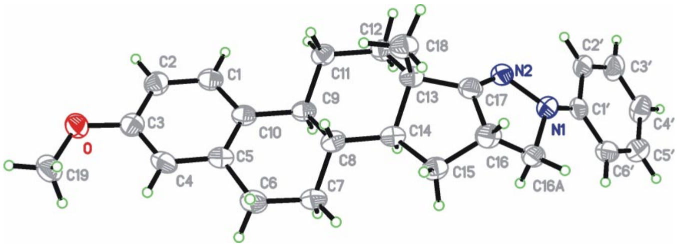


Figure 1
View of the molecule of the title compound, with the atomic numbering scheme and 50% probability displacement ellipsoids.

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