Refinement

Refinement on F
$R = 0.048$
$wR = 0.028$
$S = 1.12$
1220 reflections
138 parameters
One common U refined for all H atoms
Weighting scheme: Chebychev polynomial with parameters 22.8, −48.8, 21.3 and −18.2
$(\Delta/\sigma)_{max} = 0.06$
$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 57 (11)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (4)

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

	x	y	z	U_{eq}
C(1)	0.69460 (9)	1.0319 (1)	0.0562 (2)	0.0673
C(2)	0.6295 (1)	1.0143 (1)	0.1365 (2)	0.0694
C(3)	0.57191 (9)	0.9888 (1)	0.1853 (2)	0.0631
C(4)	0.50504 (8)	0.9396 (1)	0.2270 (2)	0.0595
C(5)	0.4618 (1)	0.9833 (2)	0.3341 (2)	0.0689
C(6)	0.3994 (1)	0.9274 (2)	0.3739 (2)	0.0763
C(7)	0.3803 (1)	0.8286 (2)	0.3064 (2)	0.0779
C(8)	0.4215 (1)	0.7858 (1)	0.1976 (2)	0.0716
C(9)	0.48462 (9)	0.8396 (1)	0.1569 (2)	0.0616
C(10)	0.53220 (9)	0.7977 (1)	0.0488 (2)	0.0651
C(11)	0.5812 (1)	0.7790 (1)	−0.0298 (2)	0.0675
C(12)	0.6471 (1)	0.7648 (2)	−0.1136 (2)	0.0770
C(13)	0.7092 (1)	0.8360 (2)	−0.0540 (2)	0.0736
C(14)	0.7015 (1)	0.9634 (2)	−0.0765 (2)	0.0790
O(1)	0.74006 (8)	1.0993 (1)	0.0929 (2)	0.0882

Table 5. *Selected geometric parameters* (Å, °) *for* (4)

C(1)—C(2)	1.440 (3)	C(6)—C(7)	1.381 (3)
C(1)—C(14)	1.495 (3)	C(7)—C(8)	1.373 (3)
C(1)—O(1)	1.213 (2)	C(8)—C(9)	1.388 (3)
C(2)—C(3)	1.200 (3)	C(9)—C(10)	1.432 (3)
C(3)—C(4)	1.427 (2)	C(10)—C(11)	1.195 (2)
C(4)—C(5)	1.387 (2)	C(11)—C(12)	1.463 (3)
C(4)—C(9)	1.411 (2)	C(12)—C(13)	1.535 (3)
C(5)—C(6)	1.385 (3)	C(13)—C(14)	1.535 (3)
C(2)—C(1)—C(14)	115.4 (2)	C(6)—C(7)—C(8)	120.9 (2)
C(2)—C(1)—O(1)	122.0 (2)	C(7)—C(8)—C(9)	120.3 (2)
C(14)—C(1)—O(1)	122.5 (2)	C(4)—C(9)—C(8)	119.1 (2)
C(1)—C(2)—C(3)	169.4 (2)	C(4)—C(9)—C(10)	117.3 (1)
C(2)—C(3)—C(4)	168.9 (2)	C(8)—C(9)—C(10)	123.6 (2)
C(3)—C(4)—C(5)	123.2 (2)	C(9)—C(10)—C(11)	166.3 (2)
C(3)—C(4)—C(9)	116.8 (2)	C(10)—C(11)—C(12)	172.6 (2)
C(5)—C(4)—C(9)	119.9 (2)	C(11)—C(12)—C(13)	111.5 (1)
C(4)—C(5)—C(6)	119.9 (2)	C(12)—C(13)—C(14)	115.0 (2)
C(5)—C(6)—C(7)	119.9 (2)	C(1)—C(14)—C(13)	115.5 (1)

The structures were solved using direct methods and successive Fourier maps (*SHELXS*86; Sheldrick, 1985) and refined using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Figures were drawn using *ORTEP* (Johnson, 1965). H-atom positions were calculated. In compound (3*a*), large displacement parameters were found for C(12), C(13) and C(14) with large standard deviations on the positional parameters. Restraints on bonds and angles were used in the refinement to obtain this part of the structure and successive refinement steps did not affect the rest of the structure. There was no evidence for disorder such as that found by Bennett & Smith (1977) for 3,4-benzocyclodeca-1,5-diyne. The slightly high R value for (3*a*) is due to the small size of the sample and the low ratio of observations to parameters.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving H atoms, along with stereoviews of the crystal packing have been deposited with the IUCr (Reference: PA1115). 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. (1995). C**51**, 721–723

3′-Methoxyspiro[bicyclo[3.1.0]hexane-6,16′-estra-1′,3′,5′(10′)-trien]-17′-one

ROB W. W. HOOFT

EMBL, Meyerhofstrasse 1, D-69117 Heidelberg, Germany

JAN KROON

Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

(*Received* 15 *February* 1994; *accepted* 1 *August* 1994)

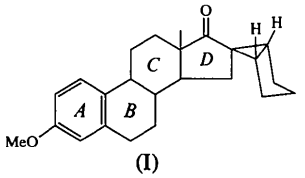
Abstract

The title compound, $C_{24}H_{30}O_2$, is a substituted steroid structure. Ring *A* is planar, ring *B* adopts a distorted half-chair conformation, ring *C* a chair conformation,

ring *D* a half-chair conformation and the trimethylene moiety of the bicyclo[3.1.0]hexane system an envelope conformation.

Comment

The structure of the title compound, (I), was determined to confirm the product of a new and unprecedented reaction by which a spirobicyclo[3.1.0]hexane moiety is formed in the α position of a ketone by treatment with 4-pentynyl triphenylphosphonium bromide (Broess, Groen & Hamersma, 1994)



(I)

Ring *A* (C1–C5, C10) is essentially planar with the C atom of the methoxy substituent 0.127 (5) Å out of the ring plane. Ring *B* (C5–C10) has a distorted 7α,8β-half-chair conformation [ΔC_2(7–8) = 10.4°], which is generally observed in estra-1,3,5(10)-trienes having a natural configuration [asymmetry parameters as in Duax & Norton (1975)]. Ring *C* (C8, C9, C11–C14) has the ususal, almost ideal, chair conformation [ΔC_s(8) = 7.1, ΔC_s(9) = 5.3 and ΔC_s(11) = 2.3°]. Ring *D* (C13–C17) is in a 13β,14α-half-chair conformation [ΔC_2(13–14) = 2.3°], whereas in estradiol conformations intermediate between a 13β-envelope and a 13β,14α-half-chair are observed (Busetta & Hospital, 1972; Busetta, Courseille, Geoffre & Hospital, 1972; Duax, 1972; van Geerestein, 1987, 1988).

There are two short C—H···O contacts involving the keto group with C···O distances of 3.45 (6) and 3.398 (2) Å, and H···O distances of 2.55 (2) and 2.59 (3) Å.

Our results also confirm the stereochemistry of the product, which has atom C15 of the steroid in an *endo* position relative to the bicyclic system.

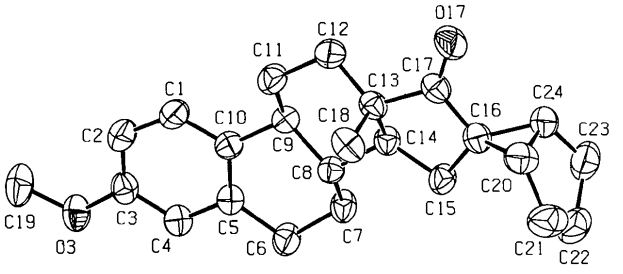


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title molecule with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are displayed as circles of arbitrary radii.

Experimental

Crystals of the title compound were obtained from Organon International, The Netherlands, and recrystallized from diethyl ether.

Crystal data

$C_{24}H_{30}O_2$
M_r = 350.50
Monoclinic
$P2_1$
a = 6.6532 (6) Å
b = 7.1539 (4) Å
c = 20.3786 (13) Å
β = 93.473 (7)°
V = 968.17 (12) Å^3
Z = 2
D_x = 1.202 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 12.47–21.20°
μ = 0.54 mm^{-1}
T = 293 (2) K
Plate-like
1.25 × 0.85 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4F diffractometer
Profile data from $\theta/2\theta$ scans
Absorption correction: by integration from crystal shape
T_{min} = 0.662, T_{max} = 0.973
4773 measured reflections
2160 independent reflections
2128 observed reflections [$I > 2.5\sigma(I)$]
R_{int} = 0.020
θ_{max} = 74.99°
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 0$
$l = -25 \rightarrow 25$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
R = 0.030
wR = 0.034
S = 0.18
2128 reflections
326 parameters
Only coordinates of H atoms refined
Calculated weights (McCandlish, Stout & Andrews,1975) with p = 0.02
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.11 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
O3	1.3279 (2)	0.38260	0.03044 (6)	0.0542 (4)
O17	0.0740 (2)	0.0902 (3)	0.32949 (8)	0.0659 (5)
C1	0.8731 (3)	0.1739 (4)	0.09316 (9)	0.0531 (6)
C2	1.0412 (3)	0.1914 (4)	0.05617 (8)	0.0540 (6)
C3	1.1596 (3)	0.3482 (3)	0.06438 (7)	0.0435 (5)
C4	1.1116 (3)	0.4835 (3)	0.10969 (8)	0.0428 (4)
C5	0.9438 (3)	0.4651 (3)	0.14706 (7)	0.0391 (4)
C6	0.9069 (3)	0.6141 (3)	0.19784 (9)	0.0477 (5)
C7	0.6986 (3)	0.6023 (3)	0.22493 (9)	0.0453 (5)
C8	0.6452 (2)	0.4002 (3)	0.24049 (7)	0.0367 (4)
C9	0.6295 (3)	0.2874 (3)	0.17588 (8)	0.0397 (4)
C10	0.8200 (2)	0.3071 (3)	0.13878 (7)	0.0403 (5)
C11	0.5679 (3)	0.0833 (3)	0.18689 (10)	0.0517 (6)
C12	0.3762 (3)	0.0643 (4)	0.22528 (9)	0.0498 (5)
C13	0.4000 (2)	0.1750 (3)	0.28894 (8)	0.0397 (4)

C14	0.4471 (2)	0.3796 (3)	0.27334 (7)	0.0388 (4)
C15	0.4104 (3)	0.4873 (4)	0.33683 (9)	0.0479 (5)
C16	0.2348 (3)	0.3800 (4)	0.36391 (7)	0.0449 (5)
C17	0.2137 (2)	0.1992 (3)	0.32745 (8)	0.0452 (5)
C18	0.5568 (3)	0.0840 (4)	0.33795 (10)	0.0525 (6)
C19	1.3937 (4)	0.2395 (5)	−0.01082 (12)	0.0689 (8)
C20	0.1855 (3)	0.3681 (4)	0.43600 (8)	0.0548 (6)
C21	0.2735 (4)	0.5146 (5)	0.48256 (10)	0.0734 (9)
C22	0.2168 (4)	0.7029 (5)	0.45177 (11)	0.0727 (8)
C23	0.0350 (4)	0.6674 (5)	0.40359 (12)	0.0698 (8)
C24	0.0411 (3)	0.4619 (4)	0.38802 (8)	0.0516 (5)

Table 2. *Selected geometric parameters* (Å, °)

O3—C3	1.374 (2)	C11—C12	1.542 (3)
O3—C19	1.411 (3)	C12—C13	1.520 (3)
O17—C17	1.216 (2)	C13—C14	1.534 (3)
C1—C2	1.392 (3)	C13—C17	1.517 (2)
C1—C10	1.392 (3)	C13—C18	1.544 (3)
C2—C3	1.375 (3)	C14—C15	1.538 (3)
C3—C4	1.388 (3)	C15—C16	1.529 (3)
C4—C5	1.395 (3)	C16—C17	1.494 (3)
C5—C6	1.516 (3)	C16—C20	1.527 (2)
C5—C10	1.403 (3)	C16—C24	1.524 (3)
C6—C7	1.525 (3)	C20—C21	1.508 (4)
C7—C8	1.527 (3)	C20—C24	1.488 (3)
C8—C9	1.542 (2)	C21—C22	1.524 (5)
C8—C14	1.5211 (19)	C22—C23	1.532 (4)
C9—C10	1.521 (2)	C23—C24	1.505 (5)
C9—C11	1.537 (3)		
C3—O3—C19	117.51 (16)	C14—C13—C17	100.48 (15)
C2—C1—C10	123.0 (2)	C14—C13—C18	113.44 (15)
C1—C2—C3	118.7 (2)	C17—C13—C18	104.76 (14)
O3—C3—C2	124.29 (16)	C8—C14—C13	112.14 (15)
O3—C3—C4	115.94 (17)	C8—C14—C15	120.51 (15)
C2—C3—C4	119.77 (18)	C13—C14—C15	105.00 (15)
C3—C4—C5	121.41 (19)	C14—C15—C16	102.47 (18)
C4—C5—C6	118.31 (18)	C15—C16—C17	107.82 (16)
C4—C5—C10	119.59 (17)	C15—C16—C20	126.07 (18)
C6—C5—C10	122.04 (16)	C15—C16—C24	127.1 (2)
C5—C6—C7	113.36 (17)	C17—C16—C20	114.3 (2)
C6—C7—C8	110.83 (16)	C17—C16—C24	115.94 (18)
C7—C8—C9	108.83 (14)	C20—C16—C24	58.40 (13)
C7—C8—C14	113.70 (16)	O17—C17—C13	126.51 (19)
C9—C8—C14	108.02 (14)	O17—C17—C16	125.96 (16)
C8—C9—C10	111.13 (15)	C13—C17—C16	107.52 (15)
C8—C9—C11	112.17 (15)	C16—C20—C21	118.0 (2)
C10—C9—C11	113.47 (17)	C16—C20—C24	60.70 (13)
C1—C10—C5	117.46 (15)	C21—C20—C24	108.1 (2)
C1—C10—C9	121.43 (18)	C20—C21—C22	106.16 (19)
C5—C10—C9	121.05 (16)	C21—C22—C23	106.5 (3)
C9—C11—C12	113.20 (18)	C22—C23—C24	105.5 (2)
C11—C12—C13	109.91 (17)	C16—C24—C20	60.90 (13)
C12—C13—C14	109.41 (15)	C16—C24—C23	118.5 (2)
C12—C13—C17	117.06 (14)	C20—C24—C23	109.05 (19)
C12—C13—C18	111.34 (18)		

The crystal used for the structure determination was unusually large, but by using an Ni β-filter instead of a monochromator on the diffractometer it was ensured that the homogeneous part of the incident X-ray beam was large enough to surround the crystal completely.

Data collection: *ARGUS* (Schreurs & Duisenberg, unpublished). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PLATON*93 (Spek, 1990). User interface software: *S* (Spek, 1994) .

We would like to thank Organon International BV for supplying the compound.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, and torsion angles have been deposited with the IUCr (Reference: AB1170). 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. (1995). C**51**, 723–726

Two Antithrombotic Quinazolone Derivatives

ZSOLT BÖCSKEI AND KÁLMÁN SIMON

Department of Chemical Research, Chinoin Pharmaceuticals, POB 110, 1325 Budapest, Hungary

LÁSZLÓ ÖRFI AND JÓZSEF KÖKÖSI

Institut for Pharmaceutical Chemistry, Semmelweis University of Medicine, Högyes E.u.9, 1092 Budapest, Hungary

(*Received* 23 *February* 1994; *accepted* 11 *April* 1994)

Abstract

The structures of two antithrombotic quinazolone derivatives, 1,2,3,5-tetrahydro-2-benzylimidazo[5,1-*b*]-quinazolin-5-one, (I), and 3-benzyl-2-[1-(2,5-xylidino)-