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Structure of (4′*R*)-4′-Methoxycarbonyl-17*β*-methoxymethyl-2,5*β*-ethanoestr-3-one, a Bridged Steroid Derivative

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Abstract. $C_{24}H_{36}O_5$, $M_r = 404\cdot55$, monoclinic, $C2$, $a = 12\cdot978\ (7)$, $b = 7\cdot076\ (5)$, $c = 24\cdot598\ (9)$ Å, $\beta = 97\cdot20\ (5)°$, $V = 2241\ (2)$ Å^3, $Z = 4$, $D_x = 1\cdot199$ Mg m^{-3}, $F(000) = 880$, $\lambda(\text{Mo}\ K\alpha) = 0\cdot71073$ Å, $\mu = 0\cdot08$ mm^{-1}, $T = 291\ (1)$ K, final $R = 0\cdot048$ for 2915 unique observed $[F \geq 3\cdot0\sigma(F)]$ diffractometer data. The reaction product of 17*β*-methoxymethylestr-4-en-3-one with methyl acrylate leads to a novel [2.2.2]bicyclooctane framework. The constitution and configuration of this product has been clarified by X-ray analysis. Surprisingly, the newly introduced methoxycarbonylethano bridge was located on the *β*-face [*syn* to the angular methyl C(18)]. The chiral center at C(4′) displays *R* configuration.

Experimental. Following the conditions of Weber, Spitzner & Kraus (1981) an excess of methyl acrylate at 205 K was added to a THF solution of 17*β*-methoxymethylestra-4-en-3-one in the presence of LDA. The product can either be interpreted as the result of a tandem Michael addition or a Diels–Alder reaction. The oily product was purified by using preparative TLC and then crystallized from methanol at 273 K, m.p. 357–358 K. Crystal size ~0·45 × 0·13 × 0·22 mm, $\omega/2\theta$ scan, scan speed 1·7–5·0° min^{-1} in θ, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; lattice parameters from least-squares fit with 25 reflections up to $2\theta = 24\cdot4°$; six standard reflections recorded every 2·5 h, only random deviations; 8124 reflections measured, $1\cdot5° \leq \theta \leq 25\cdot0°$, $-15 \leq h \leq 15$, $-8 \leq k \leq 8$, $-29 \leq l \leq 29$; after averaging ($R_{\text{int}} = 0\cdot026$): 3950 unique reflections, 2915 with $F \geq$

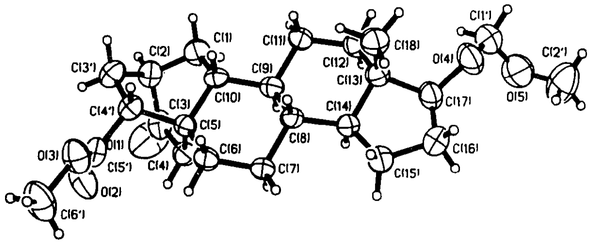

Fig. 1. General view (*SHELXTL PLUS* graphic) of the molecule, showing the atom-numbering scheme.

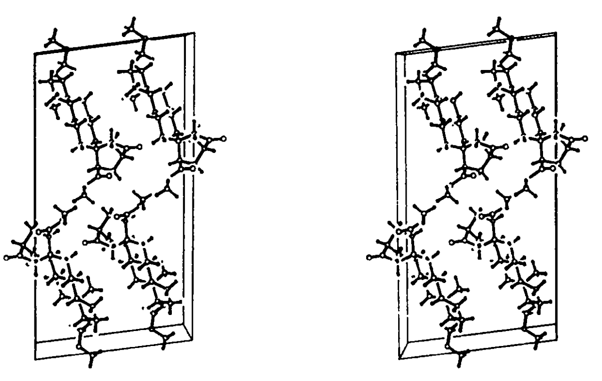

Fig. 2. Stereoscopic view (*SHELXTL PLUS* graphic) of the unit cell (*a* horizontal, *c* vertical).

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

$U_{eq} = (1/3)(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}
C(1)	0·5106 (2)	0·21308	0·3364 (1)	53
C(2)	0·5750 (2)	0·3389 (4)	0·3787 (1)	49
C(3)	0·5934 (2)	0·5219 (5)	0·3511 (1)	53
C(4)	0·4951 (2)	0·6094 (4)	0·3239 (1)	45
C(5)	0·4003 (2)	0·5048 (4)	0·3407 (1)	36
C(6)	0·2974 (2)	0·6029 (4)	0·3194 (1)	44
C(7)	0·2702 (2)	0·5887 (4)	0·2581 (1)	45
C(8)	0·2619 (2)	0·3811 (4)	0·2407 (1)	39
C(9)	0·3660 (2)	0·2817 (4)	0·2576 (1)	41
C(10)	0·4007 (2)	0·2993 (4)	0·3191 (1)	39
C(11)	0·3614 (2)	0·0740 (4)	0·2391 (1)	48
C(12)	0·3222 (2)	0·0482 (4)	0·1783 (1)	52
C(13)	0·2181 (2)	0·1475 (4)	0·1624 (1)	46
C(14)	0·2315 (2)	0·3570 (4)	0·1796 (1)	44
C(15)	0·1334 (3)	0·4517 (4)	0·1507 (1)	61
C(16)	0·1064 (3)	0·3371 (5)	0·0977 (1)	66
C(17)	0·1837 (2)	0·1725 (5)	0·1012 (1)	55
C(18)	0·1322 (2)	0·0484 (5)	0·1895 (1)	58
C(1′)	0·1990 (3)	−0·0967 (5)	0·0449 (2)	77
C(2′)	0·1231 (3)	−0·0003 (6)	−0·0410 (2)	103
C(3′)	0·5119 (2)	0·3810 (5)	0·4259 (1)	55
C(4′)	0·4112 (2)	0·4904 (4)	0·4042 (1)	42
C(5′)	0·4090 (2)	0·6812 (5)	0·4304 (1)	46
C(6′)	0·3134 (3)	0·8897 (5)	0·4804 (2)	85
O(1)	0·6770 (2)	0·5906 (5)	0·3516 (1)	113
O(2)	0·4755 (2)	0·7988 (4)	0·4309 (1)	77
O(3)	0·3243 (1)	0·7081 (4)	0·45447 (8)	60
O(4)	0·1354 (2)	0·0085 (4)	0·07502 (9)	70
O(5)	0·2142 (2)	−0·0158 (4)	−0·0043 (1)	82

$3{\cdot}0\sigma(F)$; Lorentz–polarization correction, no absorption correction; systematic absences (hkl) $h + k = 2n + 1$ conform to space groups $C2/m$, $C2$ and Cm, structure solution *via* direct methods in space group $C2$, ΔF syntheses and full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C—H 0·96 Å); refinement on F with 2915 reflections and 266 refined parameters; $w = 1{\cdot}0/[\sigma^2(F) + (0{\cdot}0005F^2)]$; $S = 1{\cdot}37$, $R = 0{\cdot}048$, $wR = 0{\cdot}045$, $(\Delta/\sigma)_{max} = 0{\cdot}14$, no extinction correction; largest peak in final ΔF map $\pm 0{\cdot}25\,(2)\ e\ Å^{-3}$, atomic scattering factors for neutral atoms and real and imaginary dispersion terms from *International Tables for X-ray Crystallography* (1974); programs: *Enraf–Nonius Structure Determination Package* (Frenz, 1985) for data reduction, *PARST* (Nardelli, 1982), *SHELXTL PLUS* (Sheldrick, 1987). The molecule and the numbering scheme are shown in Fig. 1 and a stereoscopic view of the unit cell is in Fig. 2. Positional parameters and the equivalent values of the anisotropic temperature factors for the non-H atoms are given in Table 1.* Bond lengths and angles are given in Table 2.

Table 2. *Bond distances* (Å) *and angles* (°)

C(1)—C(2)	1·535 (4)	C(12)—C(13)	1·530 (4)
C(1)—C(10)	1·560 (4)	C(13)—C(14)	1·546 (4)
C(2)—C(3)	1·495 (5)	C(13)—C(17)	1·526 (4)
C(2)—C(3′)	1·532 (5)	C(13)—C(18)	1·538 (4)
C(3)—C(4)	1·499 (4)	C(14)—C(15)	1·533 (4)
C(3)—O(1)	1·187 (4)	C(15)—C(16)	1·539 (5)
C(4)—C(5)	1·536 (4)	C(16)—C(17)	1·532 (5)
C(5)—C(6)	1·537 (4)	C(17)—O(4)	1·433 (4)
C(5)—C(10)	1·548 (4)	C(1′)—O(4)	1·391 (5)
C(5)—C(4′)	1·555 (4)	C(1′)—O(5)	1·376 (5)
C(6)—C(7)	1·508 (4)	C(2′)—O(5)	1·400 (5)
C(7)—C(8)	1·531 (4)	C(3′)—C(4′)	1·555 (4)
C(8)—C(9)	1·534 (4)	C(4′)—C(5′)	1·498 (4)
C(8)—C(14)	1·513 (4)	C(5′)—O(2)	1·198 (4)
C(9)—C(10)	1·529 (4)	C(5′)—O(3)	1·326 (4)
C(9)—C(11)	1·537 (4)	C(6′)—O(3)	1·449 (5)
C(11)—C(12)	1·530 (4)		

C(2)—C(1)—C(10)	111·1 (2)	C(11)—C(12)—C(13)	111·8 (3)
C(1)—C(2)—C(3′)	109·2 (3)	C(12)—C(13)—C(18)	110·2 (3)
C(1)—C(2)—C(3)	107·5 (2)	C(12)—C(13)—C(17)	116·5 (3)
C(3)—C(2)—C(3′)	107·9 (3)	C(12)—C(13)—C(14)	107·7 (3)
C(2)—C(3)—O(1)	123·2 (4)	C(17)—C(13)—C(18)	110·0 (3)
C(2)—C(3)—C(4)	112·7 (3)	C(14)—C(13)—C(18)	112·4 (3)
C(4)—C(3)—O(1)	124·1 (3)	C(14)—C(13)—C(17)	99·7 (2)
C(3)—C(4)—C(5)	110·3 (3)	C(8)—C(14)—C(13)	112·8 (2)
C(4)—C(5)—C(4′)	109·1 (3)	C(13)—C(14)—C(15)	103·5 (3)
C(4)—C(5)—C(10)	108·8 (3)	C(8)—C(14)—C(15)	120·6 (3)
C(4)—C(5)—C(6)	112·4 (3)	C(14)—C(15)—C(16)	104·5 (3)
C(10)—C(5)—C(4′)	106·2 (2)	C(15)—C(16)—C(17)	106·0 (3)
C(6)—C(5)—C(4′)	109·7 (3)	C(13)—C(17)—C(16)	104·6 (3)
C(6)—C(5)—C(10)	110·4 (3)	C(16)—C(17)—O(4)	110·2 (3)
C(5)—C(6)—C(7)	113·2 (3)	C(13)—C(17)—O(4)	113·9 (3)
C(6)—C(7)—C(8)	110·1 (3)	O(4)—C(1′)—O(5)	113·9 (3)
C(7)—C(8)—C(14)	112·8 (3)	C(2)—C(3′)—C(4′)	110·0 (3)
C(7)—C(8)—C(9)	109·6 (3)	C(5)—C(4′)—C(3′)	110·2 (3)
C(9)—C(8)—C(14)	109·2 (3)	C(3′)—C(4′)—C(5′)	111·2 (3)
C(8)—C(9)—C(11)	111·0 (3)	C(5)—C(4′)—C(5′)	111·6 (3)
C(8)—C(9)—C(10)	111·8 (3)	C(4′)—C(5′)—O(3)	112·5 (3)
C(10)—C(9)—C(11)	111·4 (3)	C(4′)—C(5′)—O(2)	125·3 (3)
C(5)—C(10)—C(9)	113·7 (2)	O(2)—C(5′)—O(3)	122·2 (3)
C(1)—C(10)—C(9)	112·6 (3)	C(5′)—O(3)—C(6′)	117·1 (3)
C(1)—C(10)—C(5)	108·4 (3)	C(17)—O(4)—C(1′)	114·7 (3)
C(9)—C(11)—C(12)	113·5 (3)	C(1′)—O(5)—C(2′)	113·4 (4)

There are no short contacts between the molecules. By means of X-ray analysis both the orientation of the bridge with respect to the molecular plane and the configuration of the new chiral center were clarified.

Related literature. Birch & McKague (1970) published the synthesis of a bridged *A*-ring steroid derivative, unfortunately without presenting relevant analytical data. The aim of the work reported here was the synthesis of bridged *A*-ring estradiol derivatives in connection with the determination of their configuration. In agreement with Hauser, Philip & Carroll (1973) we realized that the preparation described by Birch & McKague (1970) leads to irreproducible results. Therefore, we had to develop a new synthetic approach to the title compound (1). For the first time tandem Michael additions from the literature (Lee, 1973; Krafft & Holton, 1984; Weber, Spitzner & Kraus, 1981) have been applied to the steroid nucleus. Bridged systems in ring *B* or *D* of the steroid molecule were synthesized recently by different methods (Yates

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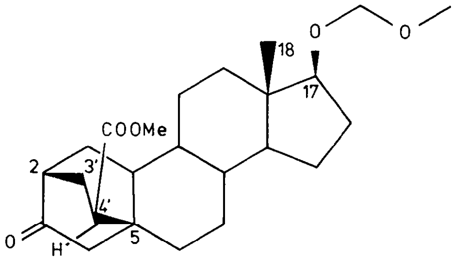
* Lists of H-atom coordinates, anisotropic thermal parameters and structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51359 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

& Walliser, 1976; Schomburg, Thielmann & Winterfeldt, 1985, 1986; Chowdhury, Prelle, Schomburg, Thielmann & Winterfeldt, 1987).



(1)

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SHORT COMMUNICATION

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Acta Cryst. (1989). C**45**, 173–174

The space group of bis(1,3-propanediamine)mercury(II) sulfate dihydrate.

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(*Received* 2 *September* 1985; *accepted* 12 *October* 1988)

Abstract

The structure of bis(1,3-propanediamine)mercury(II) sulfate dihydrate was originally presented in space group *P*2 [Kamenar, Grdenić & Hergold-Brundić (1984). *Acta Cryst.* C**40**, 1836–1838]; a more appropriate space group is *P*2/*n*.

Introduction

During the preparation of a brief review (Jones, 1986) of noncentrosymmetric structures published in *Acta Crystallographica*, Section C, 1984, it was noticed that some structures were in fact probably centrosymmetric. One such case is presented here.

Bis(1,3-propanediamine)mercury(II) sulfate dihydrate, $[Hg(C_3H_{10}N_2)_2]SO_4.2H_2O$ (Kamenar, Grdenić & Hergold-Brundić, 1984; henceforth KGH), was described in space group *P*2, with $a = 13{\cdot}830$, $b = 6{\cdot}023$, $c = 8{\cdot}250$ Å, $\beta = 97{\cdot}45°$, $Z = 2$; two independent Hg and two independent S atoms lay on twofold axes. Inspection of the atomic coordinates of KGH shows that the structure is to a good approximation centrosymmetric; a coordinate shift of *ca* 0·25, 0·48, 0·25 leads to atom positions corresponding closely to space group *P*2/*n*. Refinement on *F* of the *P*2/*n* structure using the deposited structure factors (1893 reflections, unit weights, Hg and S anisotropic) gives an *R* value of 0·038 for 43 parameters (*cf.* KGH: $R = 0{\cdot}033$ for a weighted refinement, all atoms anisotropic, 164 parameters). The reflections $h0l$, $h + l$ odd, are required to be systematically absent in *P*2/*n*; 20 such reflections are present in the list of observed structure factors, but all are weak. The max. Δ/σ in the final cycle was 0·001.

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