

Two 17-hydroxy-9(10→5)-*abeo*-estr-4-ene-3,10-diones

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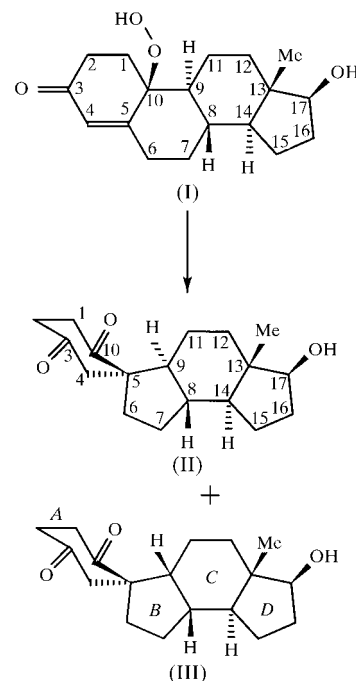
(5*S*,9*S*,17*S*)-17-Hydroxy-9(10→5)-*abeo*-estr-4-ene-3,10-dione, C<sub>18</sub>H<sub>26</sub>O<sub>3</sub>, (II), and (5*R*,9*R*,17*S*)-17-hydroxy-9(10→5)-*abeo*-estr-4-ene-3,10-dione, C<sub>18</sub>H<sub>26</sub>O<sub>3</sub>, (III), are equimolecular products of the Fe<sup>II</sup>-induced transposition of 10β-hydroperoxy-17β-hydroxyestr-4-en-3-one, (I). With respect to reagent molecules, the configuration at C9 is retained for (II) while it is inverted in (III). The conformations of the five- and six-membered rings are compared.

## Comment

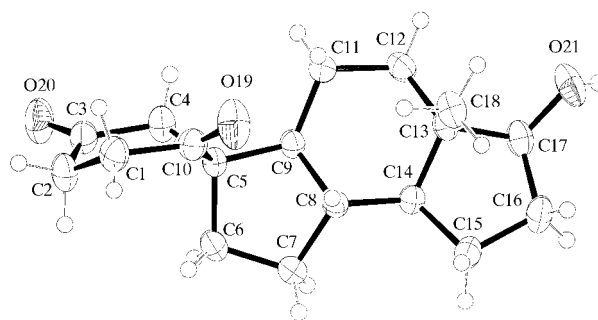
The title compounds were synthesized and crystallized according to the procedure described by Canonica *et al.* (1987) for similar steroids (see Scheme below). The present crystallographic study was undertaken in order to determine the configuration of the two compounds at the C9 atom.

Both structures present no unusual bond lengths and angles. The two molecules are shown in Figs. 1 and 2; the numbering scheme derives from estrene. In (II), the two H atoms bonded at C8 and C9 are *anti*, as in the parent compound, while in (III) they are *syn*. In (II), ring A (C1–C5/C10, see Scheme) presents a B<sub>2,5</sub> conformation [according to the notation of Boeyens (1978)], with  $Q_{\text{tot}} = 0.605$  (2) Å,  $\varphi_2 = 56.1$  (2)° and  $\theta_2 = 98.7$  (2)° [Cremer & Pople (1975), calculated following Nardelli (1983)], ring C (C8/C9/C11–C14) has a regular chair conformation [ $Q_{\text{tot}} = 0.580$  (2) Å,  $\varphi_2 = -99.0$  (3)° and  $\theta_2 = 3.8$  (2)°], as found in similar steroids such as GEMYUS [(5*S*)-9(10→5)-*abeo*-1-estrene-3,10,17-trione; Piniella & Rius, 1988], ring B (C5–C9) shows a <sup>5</sup>T<sub>4</sub> conformation [ $Q_{\text{tot}} = 0.444$  (2) Å and  $\varphi_2 = 131.6$  (2)°], as in GEMYUS, and finally, ring D (C13–C17) has a distorted envelope (*E*<sub>1</sub>) conformation [ $Q_{\text{tot}} = 0.474$  (2) Å and  $\varphi_2 = -172.3$  (2)°]. In (III), only ring D [ $Q_{\text{tot}} = 0.462$  (3) Å and  $\varphi_2 = -175.2$  (4)°] has the same conformation found in (II). In all other cases, there are strong differences: ring A presents a conformation between <sup>4</sup>T<sub>2</sub> and <sup>1,4</sup>B [ $Q_{\text{tot}} = 0.657$  (3) Å,  $\varphi_2 = 20.2$  (2)° and  $\theta_2 = 92.5$  (3)°], ring C has a chair conformation noticeably distorted in the <sup>5</sup>E direction [ $Q_{\text{tot}} = 0.507$  (2) Å,  $\varphi_2 = -125.5$  (7)° and  $\theta_2 = 28.6$  (3)°] and ring B shows a distorted

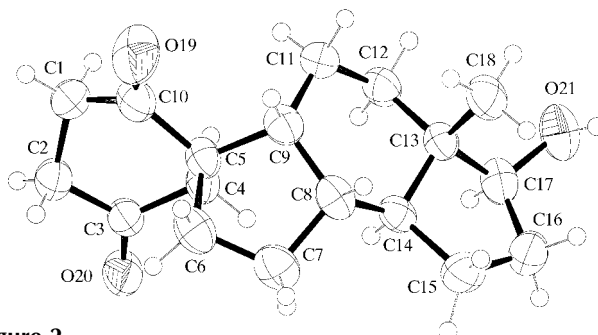
<sup>1</sup>T<sub>2</sub> conformation [ $Q_{\text{tot}} = 0.415$  (3) Å and  $\varphi_2 = 11.8$  (4)°]. Most likely these conformational differences are mainly due to the



intramolecular O19...H9 interaction [2.42 (3) Å], which is present in (III), but not in (II). The main packing interaction, both in (II) and (III), is the H21...O20<sup>i</sup> hydrogen bond, where (i) is  $-\frac{1}{2} - x, -y, z - \frac{1}{2}$  for (II), and  $-x, y - \frac{1}{2}, \frac{1}{2} - z$  for (III);



**Figure 1**  
ORTEP (Burnett & Johnson, 1996) projection of (II). Ellipsoids are at the 50% probability level and H atoms are not to scale.



**Figure 2**  
ORTEP (Burnett & Johnson, 1996) projection of (III). Ellipsoids are at the 50% probability level and H atoms are not to scale.

the distances O··O<sup>i</sup> and H··O<sup>i</sup>, and the corresponding O—H··O<sup>i</sup> angle measure 2.863 (2), 2.05 (2) Å and 174 (2)° for (II), and 2.862 (3), 2.03 (4) Å and 150 (4)° for (III).

## Experimental

The title compounds were synthesized and crystallized according to the procedure described by Canonica *et al.* (1987) for similar steroids.

### Compound (II)

#### Crystal data

C<sub>18</sub>H<sub>26</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 290.39  
 Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 6.5843 (5) Å  
*b* = 10.4040 (7) Å  
*c* = 22.3443 (12) Å  
*V* = 1530.65 (18) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.260 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 52 reflections  
 $\theta$  = 5.17–14.75°  
 $\mu$  = 0.084 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Cubic, colourless  
 0.32 × 0.30 × 0.30 mm

#### Data collection

Bruker *P4* diffractometer  
 2 $\theta$ / $\omega$  scans  
 5088 measured reflections  
 2577 independent reflections  
 2216 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.018  
 $\theta$ <sub>max</sub> = 30.0°

*h* = 0 → 9  
*k* = 0 → 14  
*l* = 0 → 31  
 3 standard reflections every 197 reflections  
 intensity decay: none

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.035  
*wR* (*F*<sup>2</sup>) = 0.086  
*S* = 0.979  
 2577 reflections  
 295 parameters  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0474P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = 0.01  
 $\Delta\rho$ <sub>max</sub> = 0.24 e Å<sup>-3</sup>  
 $\Delta\rho$ <sub>min</sub> = -0.13 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97* (Sheldrick, 1997)  
 Extinction coefficient: 0.0151 (19)  
 Absolute structure: based on the reagents configuration

### Compound (III)

#### Crystal data

C<sub>18</sub>H<sub>26</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 290.39  
 Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 6.6278 (5) Å  
*b* = 11.1491 (9) Å  
*c* = 21.1609 (19) Å  
*V* = 1563.7 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.234 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 60 reflections  
 $\theta$  = 3.70–12.49°  
 $\mu$  = 0.082 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Squared prism, colourless  
 0.34 × 0.24 × 0.22 mm

#### Data collection

Bruker *P4* diffractometer  
 2 $\theta$ / $\omega$  scans  
 4127 measured reflections  
 2094 independent reflections  
 1400 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.026  
 $\theta$ <sub>max</sub> = 27.5°

*h* = 0 → 8  
*k* = 0 → 14  
*l* = 0 → 27  
 3 standard reflections every 197 reflections  
 intensity decay: none

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.039  
*wR* (*F*<sup>2</sup>) = 0.092  
*S* = 0.960  
 2094 reflections  
 295 parameters  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = 0.002  
 $\Delta\rho$ <sub>max</sub> = 0.12 e Å<sup>-3</sup>  
 $\Delta\rho$ <sub>min</sub> = -0.13 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97* (Sheldrick, 1997)  
 Extinction coefficient: 0.011 (2)  
 Absolute structure: based on the reagents configuration

Refined C—H distances are in the ranges 0.90 (2)–1.02 (2) Å and 0.91 (3)–1.08 (3) Å for (I) and (II), respectively.

For both compounds, data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* and *PARSTCIF* (Nardelli, 1991) for compound (II) and *SHELXL97* for compound (III).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1501). Services for accessing these data are described at the back of the journal.

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