

2306 measured reflections  
2213 independent reflections  
1626 observed reflections  
[ $I > 2\sigma(I)$ ]

3 standard reflections  
monitored every 100  
reflections  
intensity decay: none

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0606$   
 $wR(F^2) = 0.1666$   
 $S = 1.157$   
2213 reflections  
238 parameters  
H atoms refined with riding  
model  
 $w = 1/[\sigma^2(F_o^2) + (0.1349P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.561$   
 $\Delta\rho_{\max} = 0.284 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.389 \text{ e } \text{Å}^{-3}$   
Extinction correction: none  
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 ( $\text{Å}^2$ )**

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

	x	y	z	$U_{\text{eq}}$
C(1)	0.6725 (3)	0.3233 (2)	0.2109 (2)	0.0382 (7)
C(2)	0.6876 (3)	0.2023 (2)	0.2094 (2)	0.0355 (6)
C(3)	0.5701 (3)	0.1370 (2)	0.1498 (2)	0.0345 (6)
C(4)	0.4330 (3)	0.1911 (2)	0.0923 (2)	0.0355 (7)
C(5)	0.4167 (3)	0.3118 (2)	0.0904 (2)	0.0338 (6)
C(6)	0.2820 (3)	0.3712 (2)	0.0232 (2)	0.0400 (7)
C(7)	0.2819 (3)	0.5005 (2)	0.0202 (2)	0.0371 (7)
C(8)	0.1583 (4)	0.5576 (3)	-0.0429 (2)	0.0458 (7)
C(9)	0.1550 (4)	0.6773 (3)	-0.0450 (2)	0.0533 (8)
C(10)	0.2750 (4)	0.7404 (3)	0.0160 (2)	0.0547 (9)
C(11)	0.3981 (4)	0.6845 (2)	0.0793 (2)	0.0473 (8)
C(12)	0.4026 (3)	0.5645 (2)	0.0822 (2)	0.0392 (7)
C(13)	0.5340 (3)	0.5056 (2)	0.1507 (2)	0.0392 (7)
C(14)	0.5398 (3)	0.3778 (2)	0.1521 (2)	0.0361 (7)
C(15)	0.8373 (3)	0.1420 (2)	0.2688 (2)	0.0423 (7)
C(16)	0.7639 (3)	-0.0247 (2)	0.2020 (2)	0.0390 (7)
C(17)	0.5941 (3)	0.0084 (2)	0.1452 (2)	0.0385 (7)
C(18)	0.1785 (4)	0.0952 (3)	0.0520 (2)	0.0603 (9)
C(19)	0.7972 (4)	-0.1527 (2)	0.2109 (2)	0.0511 (8)
O(1)	0.7941 (3)	0.3804 (2)	0.2705 (2)	0.0560 (7)
O(2)	0.3254 (2)	0.1191 (2)	0.03280 (14)	0.0453 (6)
O(3)	0.1718 (3)	0.3191 (2)	-0.0304 (2)	0.0630 (7)
O(4)	0.6390 (3)	0.5626 (2)	0.20516 (15)	0.0542 (6)
O(5)	0.9512 (2)	0.1249 (2)	0.22160 (15)	0.0528 (6)
O(6)	0.8750 (2)	0.0304 (2)	0.16112 (14)	0.0507 (6)
O(7)	0.7990 (2)	0.0275 (2)	0.28752 (13)	0.0455 (6)

**Table 2. Selected geometric parameters ( $\text{Å}$ )**

C(1)—O(1)	1.348 (3)	C(8)—C(9)	1.383 (4)
C(1)—C(14)	1.386 (4)	C(9)—C(10)	1.385 (5)
C(1)—C(2)	1.405 (4)	C(10)—C(11)	1.375 (4)
C(2)—C(3)	1.377 (4)	C(11)—C(12)	1.387 (4)
C(2)—C(15)	1.518 (4)	C(12)—C(13)	1.471 (4)
C(3)—C(4)	1.401 (4)	C(13)—O(4)	1.231 (3)
C(3)—C(17)	1.505 (4)	C(13)—C(14)	1.477 (4)
C(4)—O(2)	1.377 (3)	C(15)—O(7)	1.416 (3)
C(4)—C(5)	1.401 (4)	C(15)—O(5)	1.420 (4)
C(5)—C(14)	1.423 (4)	C(16)—O(7)	1.411 (3)
C(5)—C(6)	1.480 (4)	C(16)—O(6)	1.459 (3)
C(6)—O(3)	1.220 (3)	C(16)—C(19)	1.506 (4)
C(5)—C(7)	1.495 (4)	C(16)—C(17)	1.521 (4)
C(7)—C(8)	1.383 (4)	C(18)—O(2)	1.429 (4)
C(7)—C(12)	1.401 (4)	O(5)—O(6)	1.463 (3)

H atoms were included in calculated positions and allowed to ride on the atom to which they were attached. H-atom displacement parameters were taken as 20% greater than those of the parent atom.

Data collection: CAD-4 software. Cell refinement: CAD-4 software. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

We thank Dr D. Larsen for provision of the crystals.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: FG1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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**A [5.5.5]Fenestrane Derivative**

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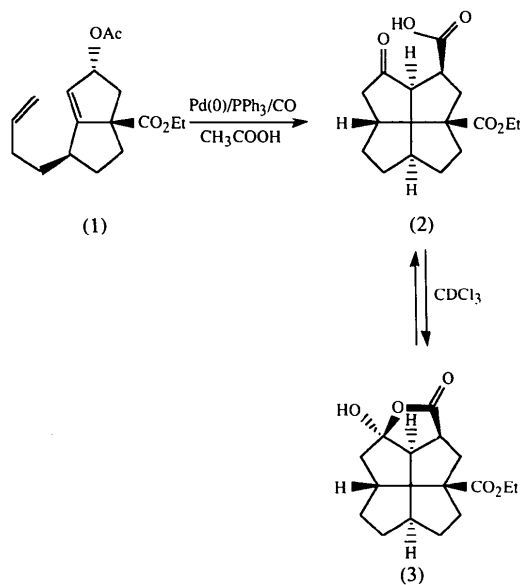
**Abstract**

The title compound, ethyl *rel*-(1*R*,2*S*,4*R*,7*R*,10*R*,12*S*)-1-hydroxy-3-oxo-2-oxapentacyclo[7.4.2.0<sup>4,14</sup>.0<sup>12,15</sup>.0<sup>6,15</sup>]-pentadecane-6-carboxylate, C<sub>17</sub>H<sub>22</sub>O<sub>5</sub>, has been synthe-

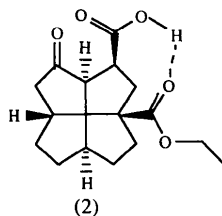
sized and its structure determined. The geometry about the central C atom of the fenestrane skeleton shows significant distortion from ideal tetrahedral towards planarity. In the hemiacetal portion of the molecule, the C—O bond in the lactone moiety is longer than the C—OH bond; this can be related to the pseudoacid–ketoacid equilibrium observed in solution and to an anomeric effect.

### Comment

Recently, several methods involving transition metals have been used to synthesize novel fenestrans (Thommen, Gerber & Keese, 1991; van der Waals & Keese, 1992; Keese, Guidetti-Grept & Herzog, 1992). One method, the palladium-catalyzed carbonylation–cyclization of the bicycle (1), yields the ketoacid (2) which, in CDCl<sub>3</sub> solution, exists in equilibrium with the pseudoacid (3) (Keese, Guidetti-Grept & Herzog, 1992). In several examples of this type of isomerization, the pseudoacid is favoured (Pfenninger, 1978; Chadwick & Dunitz, 1979).



In the present case, however, the <sup>1</sup>H and <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> solution show a 1:1 ratio of the two isomers, probably because the ketoacid is stabilized by an intramolecular hydrogen-bond interaction (see scheme below). Crystallization from ether by slow evaporation at room temperature gives exclusively the pseudoacid (3) (Figs. 1 and 2).



The structure of (3) shows two interesting features: the angles around the central C atom and the unequal lengths of hemiacetal C—O bonds (Table 2).

The connectivities in the fenestrane skeleton force a deformation of the tetrahedral angles around the central atom in the direction of planar bonding. Angles C(4)—C(13)—C(10) and C(1)—C(13)—C(7) are 119.1 (2) and 117.3 (2)°, respectively. The largest deviations obtained so far are 129.2 (5) and 128.3 (6)° in the [4.4.4.5]fenestrane series (Rao, George, Wolff & Agosta, 1985).

The C(12)—O(3) distance [1.460 (3) Å] is longer than usual (1.42 Å), whereas the C(12)—O(5) bond [1.384 (3) Å] is shorter than a typical C—OH bond (1.43 Å). Angles O(3)—C(12)—C(1) and O(3)—C(12)—C(11) are smaller [104.0 (2) and 109.9 (2)°, respectively] than O(5)—C(12)—C(1) and O(5)—C(12)—C(11) [116.8 (2) and 111.0 (2)°, respectively]. These results can be interpreted as a consequence of the isomerization of (3) to (2): the C—OH bond will become a C=O bond and the lactone C—O bond will be cleaved. An anomeric effect (Deslongchamps,

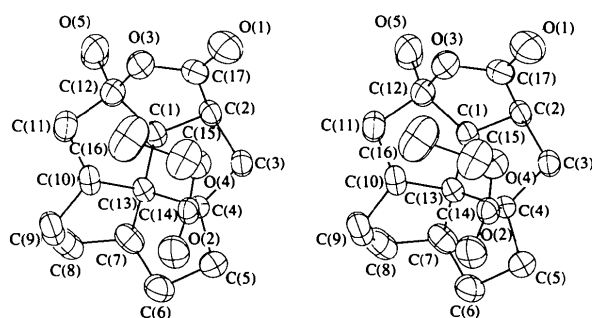


Fig. 1. Stereoscopic PEANUT (Hummel, Hauser & Bürgi, 1990) view of (3) with r.m.s. displacements (scale 1.54 corresponding to 50% probability).

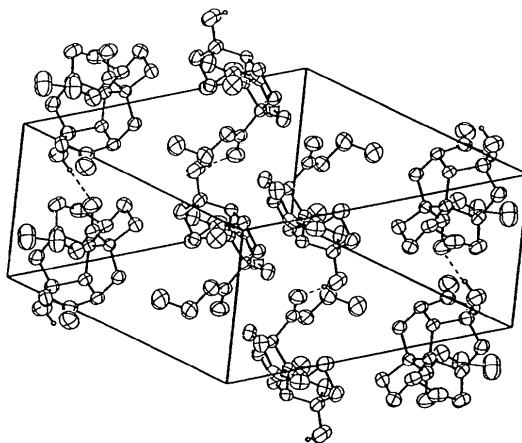


Fig. 2. Packing arrangement of (3). The broken lines indicate the hydrogen bonds giving rise to chains of molecules along the crystal *b* axis.

1983) could also be invoked to interpret these anomalous lengths: the torsion angle H—O(5)—C(12)—O(3) is 66.5 (18)°; this allows a  $\sigma^*-1p$  interaction between the C(12)—O(3)  $\sigma^*$  orbital and the antiperiplanar lone pair on O(5). The interaction is bonding between O(5) and C(12) and antibonding between C(12) and O(3), in agreement with the observed shortening and lengthening, respectively. Similar isomerization has been observed and studied crystallographically by Chadwick & Dunitz (1979); they made similar structural observations.

## Experimental

### Crystal data

C<sub>17</sub>H<sub>22</sub>O<sub>5</sub>  
*M<sub>r</sub>* = 306.36  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 13.274 (4) Å  
*b* = 7.746 (2) Å  
*c* = 15.080 (5) Å  
 $\beta$  = 108.33 (3)°  
*V* = 1472 (1) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.37 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 20 reflections  
 $\theta$  = 11–19.5°  
 $\mu$  = 0.10 mm<sup>-1</sup>  
*T* = 293 K  
 Plate  
 0.3 × 0.3 × 0.18 mm  
 Colorless  
 Crystal source: synthesis

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction: empirical  
*T<sub>min</sub>* = 0.9213, *T<sub>max</sub>* = 0.9998  
 2921 measured reflections  
 2245 independent reflections  
 1696 observed reflections  
 [*I* > 3.0σ(*I*)]

*R<sub>int</sub>* = 0.015  
 $\theta_{\max}$  = 25°  
 $h = 0 \rightarrow 13$   
 $k = 0 \rightarrow 9$   
 $l = -10 \rightarrow 10$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 0.3%

### Refinement

Refinement on *F*  
*R* = 0.040  
 $wR$  = 0.055  
*S* = 1.534  
 1696 reflections  
 205 parameters  
 Only H-atom *U*'s refined  
 $w = 1/[\sigma^2(F) + 0.000727F^2]$

$(\Delta/\sigma)_{\max}$  = 0.001  
 $\Delta\rho_{\max}$  = 0.203 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.228 e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$B_{\text{iso}} \text{ for H; } B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \text{ for others.}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>iso</sub>/B<sub>eq</sub></i>
C(1)	0.2326 (2)	0.3864 (3)	0.4150 (2)	2.81 (4)
C(2)	0.3514 (2)	0.4053 (3)	0.4629 (2)	3.03 (4)
C(3)	0.4037 (2)	0.2441 (3)	0.4389 (2)	3.22 (4)
C(4)	0.3199 (2)	0.0981 (3)	0.4151 (2)	2.72 (4)
C(5)	0.3143 (2)	0.0043 (4)	0.3235 (2)	4.03 (5)
C(6)	0.1968 (2)	-0.0248 (3)	0.2743 (2)	4.12 (5)

C(7)	0.1446 (2)	0.1411 (3)	0.2930 (2)	3.51 (4)
C(8)	0.0306 (2)	0.1159 (3)	0.2919 (2)	4.33 (5)
C(9)	0.0411 (2)	0.0381 (3)	0.3859 (2)	4.01 (5)
C(10)	0.1327 (2)	0.1395 (3)	0.4534 (2)	3.05 (4)
C(11)	0.0956 (2)	0.3094 (3)	0.4833 (2)	4.03 (5)
C(12)	0.1805 (2)	0.4394 (3)	0.4882 (2)	3.57 (5)
C(13)	0.2080 (2)	0.1918 (3)	0.3944 (2)	2.58 (4)
C(14)	0.3346 (2)	-0.0309 (3)	0.4930 (2)	3.04 (5)
C(15)	0.3907 (3)	-0.0662 (4)	0.6598 (2)	5.63 (7)
C(16)	0.3029 (3)	-0.0438 (5)	0.6966 (2)	7.01 (9)
C(17)	0.3618 (2)	0.4184 (3)	0.5647 (2)	3.57 (5)
O(1)	0.4419 (2)	0.4248 (3)	0.6292 (1)	5.48 (4)
O(2)	0.3071 (2)	-0.1800 (2)	0.4812 (1)	4.76 (4)
O(3)	0.2656 (1)	0.4228 (2)	0.5769 (1)	4.25 (4)
O(4)	0.3777 (1)	0.0382 (2)	0.5764 (1)	4.14 (3)
O(5)	0.1409 (2)	0.6058 (2)	0.4823 (2)	5.20 (5)
H	0.193 (2)	0.675 (4)	0.478 (2)	4.5 (1)

Table 2. Selected geometric parameters (Å, °)

O(3)—C(12)	1.460 (3)	C(4)—C(13)	1.593 (3)
O(5)—C(12)	1.384 (3)	C(7)—C(13)	1.546 (3)
C(1)—C(13)	1.553 (3)	C(10)—C(13)	1.585 (4)
O(3)—C(12)—O(5)	108.1 (2)	C(1)—C(13)—C(4)	106.2 (2)
O(3)—C(12)—C(1)	104.0 (2)	C(1)—C(13)—C(7)	117.3 (2)
O(3)—C(12)—C(11)	109.9 (2)	C(1)—C(13)—C(10)	105.4 (2)
O(5)—C(12)—C(1)	116.8 (2)	C(4)—C(13)—C(7)	105.2 (2)
O(5)—C(12)—C(11)	111.0 (2)	C(4)—C(13)—C(10)	119.1 (2)
C(1)—C(12)—C(11)	106.8 (2)	C(7)—C(13)—C(10)	104.2 (2)
O(3)—C(12)—O(5)—H	66.5 (18)		

Data collection: CAD-4 (Enraf–Nonius, 1989). Cell refinement: CAD-4. Data reduction: SDP (Enraf–Nonius, 1985). Programs used to solve and refine structure: SHELXTL-Plus (Sheldrick, 1991). Molecular graphics: PEANUT (Hummel, Hauser & Bürgi, 1990).

We thank the Schweizerische Nationalfonds for support. This work was undertaken during an introductory class into X-ray structure determination.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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