All H-atom parameters refined
$w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{\max} = 0.03$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| O1 | 0.2873 (1) | −0.09367 (6) | 0.5641 (1) | 5.53 (3) |
| O2 | 0.5932 (2) | −0.18533 (7) | 0.6025 (2) | 5.85 (3) |
| C1 | 0.4041 (2) | −0.04253 (8) | 0.6606 (2) | 4.07 (3) |
| C2 | 0.3568 (2) | 0.03807 (8) | 0.7242 (2) | 3.88 (3) |
| C3 | 0.1789 (2) | 0.07667 (9) | 0.6942 (2) | 4.74 (3) |
| C4 | 0.1736 (2) | 0.1528 (1) | 0.7720 (2) | 5.20 (4) |
| C5 | 0.3423 (2) | 0.1893 (1) | 0.8773 (2) | 5.44 (4) |
| C6 | 0.5194 (2) | 0.1513 (1) | 0.9074 (2) | 4.92 (3) |
| C7 | 0.5267 (2) | 0.07473 (8) | 0.8297 (2) | 3.88 (3) |
| C8 | 0.6991 (2) | 0.02053 (9) | 0.8412 (2) | 4.15 (3) |
| C9 | 0.6090 (2) | −0.05352 (8) | 0.7305 (2) | 3.82 (3) |
| C10 | 0.6966 (2) | −0.12438 (9) | 0.7019 (2) | 4.33 (3) |
| C11 | 0.9062 (2) | −0.1414 (1) | 0.7745 (2) | 5.78 (4) |

Table 2. *Geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| O1—C1 | 1.257 (2) | C4—C5 | 1.383 (2) |
| O2—C10 | 1.334 (2) | C5—C6 | 1.380 (2) |
| C1—C2 | 1.469 (2) | C6—C7 | 1.385 (2) |
| C1—C9 | 1.434 (2) | C7—C8 | 1.509 (2) |
| C2—C3 | 1.390 (2) | C8—C9 | 1.503 (2) |
| C2—C7 | 1.391 (2) | C9—C10 | 1.359 (2) |
| C3—C4 | 1.376 (2) | C10—C11 | 1.481 (2) |
| O2—H2O | 1.00 (2) | | |
| C1—C9—C8 | 110.0 (1) | C10—O2—H2O | 107 (1) |
| O2—C10—C11 | 114.8 (1) | C2—C1—C9 | 107.7 (1) |
| C7—C8—C9 | 102.56 (9) | | |
| C1—C2—C7—C8 | 0.6 (2) | C1—C9—C10—O2 | 1.9 (2) |
| O1—C1—C9—C10 | −2.4 (2) | C8—C9—C10—C11 | −1.5 (2) |

The crystal was sealed in a capillary to prevent sublimation. Programs used were *MolEN* (Fair, 1990) and *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry involving H atoms, complete geometry for non-H atoms and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71198 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1038]

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# Structure of 23,24-Dinor-5$\alpha$-cholan-12-one

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## Abstract

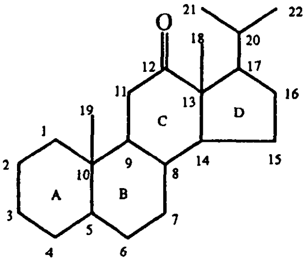
The crystal and molecular structure of 23,24-dinor-5$\alpha$-cholan-12-one has been determined. Rings *A*, *B* and *C* have a chair conformation, ring *D* a half-chair conformation. All rings are *trans* connected. The crystal structure of the title compound confirms the link between a different kinetic behaviour during reduction of 12-oxosteroids with $LiAlH_4$ and a different orientation of the $\pi$ system of the ketone functional group.

## Comment

This paper forms part of a study on complex hydride reductions of 12-oxosteroids.

It has been reported that for $LiAlH_4$ the attack of a hydride is preferentially antiperiplanar with neighbouring axial protons (Biesemans, Van de Woude & van Hove, 1990). A conformation that makes such an antiperiplanar axial attack impossible would therefore show different kinetic properties towards complex hydride reduction.

Comparison of the kinetic data on C(17)-unsubstituted 12-oxosteroids and these C(17)-substituted ones reveals a diminished velocity of axial attack for the substituted steroids that cannot be explained on steric grounds. Therefore a change in conformation of the *C* ring on introduction of the C(17) substituent is suggested. NMR data confirm this observation in the solution state. To verify whether this is also observed in the solid state we determined the crystal structure of 23,24-dinor-5$\alpha$-cholan-12-one (1).



(1)

In the crystal structure, all bond lengths and angles compare well with those found in similar structures. The distortions around C(12) are less than might be expected from its $sp^2$ hybridization. The crystallographic structure gives a clear view of the environment of the $\pi$ system of the C=O moiety. The distance between the closest H atom of C(21) and the O atom is 2.72 Å. The closeness of the C(21) methyl group forces the carbonyl into a position where axial attack of the hydride (on the $\alpha$ side of the steroid) cannot be antiperiplanar with the C(11) axial proton, thus explaining the kinetic data and confirming the observation that the conformation of the steriods in the solid state is comparable with the solution conformation (Maes, Van Cauteren, Wyns, Lisgarten, Palmer, Lisgarten, Willem, Biesemans & Kayser, 1992).

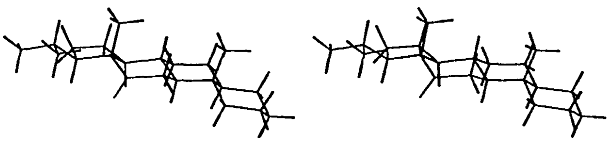


Fig. 1. Stereoview of the molecule.

## Experimental

*Crystal data*

$C_{22}H_{36}O$
$M_r = 316.5$
Monoclinic
$P2_1$
$a = 7.244$ (7) Å
$b = 9.959$ (9) Å
$c = 13.727$ (1) Å
$\beta = 102.2$ (1)°
$V = 967.86$ (4) Å$^3$
$Z = 2$
$D_x = 1.08$ Mg m$^{-3}$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 25$–28°
$\mu = 4.12$ mm$^{-1}$
$T = 293$ K
Flat plate
3.0 × 1.0 × 0.3 mm
Transparent

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4152 measured reflections
2053 independent reflections
2053 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.017$
$\theta_{\rm max} = 73°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 9$
$l = -17 \rightarrow 17$
2 standard reflections monitored every 100 reflections intensity variation: 4%

*Refinement*

Refinement on $F^2$
Final $R = 0.0491$
$wR = 0.0617$
2053 reflections
249 parameters
Only H-atom $U$'s refined
$w = [\sigma^2(F) + 0.006363F^2]^{-1}$

$(\Delta/\sigma)_{\rm max} = -0.568$
$\Delta\rho_{\rm max} = 0.21$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.20$ e Å$^{-3}$
Atomic scattering factors from *SHELX76* and *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Atomic positional parameters and equivalent isotropic temperature factors* (Å$^2$) *for the non*-H *atoms with e.s.d.'s in parentheses*

$U_{\rm eq} = (U_1U_2U_3)^{1/3}$.

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| C(1) | −0.0357 (4) | 0.1029 (6) | 0.7109 (2) | 0.0568 (4) |
| C(2) | −0.1177 (4) | 0.1019 (7) | 0.5981 (2) | 0.0708 (6) |
| C(3) | 0.0413 (5) | 0.1160 (7) | 0.5398 (2) | 0.0766 (7) |
| C(4) | 0.1946 (5) | 0.0115 | 0.5719 (2) | 0.0713 (6) |
| C(5) | 0.2748 (3) | 0.0161 (5) | 0.6851 (1) | 0.0518 (4) |
| C(6) | 0.4414 (3) | −0.0783 (6) | 0.7194 (2) | 0.0601 (4) |
| C(7) | 0.5315 (3) | −0.0552 (6) | 0.8283 (2) | 0.0507 (4) |
| C(8) | 0.3875 (3) | −0.0670 (5) | 0.8957 (1) | 0.0393 (3) |
| C(9) | 0.2139 (3) | 0.0218 (5) | 0.8569 (1) | 0.0379 (3) |
| C(10) | 0.1179 (3) | −0.0041 (5) | 0.7458 (1) | 0.0454 (3) |
| C(11) | 0.0731 (3) | 0.0158 (5) | 0.9274 (1) | 0.0451 (3) |
| C(12) | 0.1743 (3) | 0.0492 (5) | 1.0341 (1) | 0.0405 (3) |
| C(13) | 0.3387 (2) | −0.0430 (5) | 1.0761 (1) | 0.0361 (3) |
| C(14) | 0.4732 (2) | −0.0237 (5) | 1.0021 (1) | 0.0377 (3) |
| C(15) | 0.6554 (3) | −0.0877 (5) | 1.0568 (2) | 0.0534 (4) |
| C(16) | 0.6637 (3) | −0.0552 (6) | 1.1673 (2) | 0.0553 (4) |
| C(17) | 0.4666 (3) | −0.00009 (5) | 1.1765 (1) | 0.0409 (3) |
| C(18) | 0.2717 (3) | −0.1896 (5) | 1.0786 (2) | 0.0478 (3) |
| C(19) | 0.0308 (4) | −0.1446 (6) | 0.7319 (2) | 0.0601 (4) |
| C(20) | 0.4106 (3) | −0.0480 (6) | 1.2731 (1) | 0.0516 (4) |
| C(21) | 0.2155 (4) | −0.0009 (6) | 1.2843 (2) | 0.0686 (5) |
| C(22) | 0.5608 (4) | −0.0034 (7) | 1.3642 (2) | 0.0739 (6) |
| O(1) | 0.1318 (3) | 0.1478 (5) | 1.0766 (1) | 0.0586 (3) |

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1.536 (3) | C(10)—C(19) | 1.531 (3) |
| C(1)—C(10) | 1.542 (3) | C(11)—C(12) | 1.530 (2) |
| C(2)—C(3) | 1.541 (4) | C(12)—C(13) | 1.518 (2) |
| C(3)—C(4) | 1.518 (6) | C(13)—C(14) | 1.561 (2) |
| C(4)—C(5) | 1.540 (3) | C(13)—C(17) | 1.547 (2) |
| C(5)—C(6) | 1.523 (4) | C(13)—C(18) | 1.541 (2) |
| C(5)—C(10) | 1.556 (3) | C(14)—C(15) | 1.514 (4) |
| C(6)—C(7) | 1.517 (3) | C(15)—C(16) | 1.540 (3) |
| C(7)—C(8) | 1.538 (2) | C(16)—C(17) | 1.556 (3) |
| C(8)—C(9) | 1.537 (2) | C(17)—C(20) | 1.540 (3) |
| C(8)—C(14) | 1.523 (2) | C(20)—C(21) | 1.527 (3) |
| C(9)—C(10) | 1.558 (2) | C(20)—C(22) | 1.539 (3) |
| C(9)—C(11) | 1.549 (2) | C(12)—O(1) | 1.214 (3) |
| C(10)—C(1)—C(2) | 114.1 (2) | C(12)—C(11)—C(9) | 110.2 (1) |
| C(3)—C(2)—C(1) | 110.5 (2) | C(13)—C(12)—C(11) | 114.7 (2) |
| C(4)—C(3)—C(2) | 111.6 (3) | C(14)—C(13)—C(12) | 103.1 (1) |
| C(3)—C(4)—C(5) | 111.7 (3) | C(17)—C(13)—C(12) | 116.6 (2) |
| C(6)—C(5)—C(4) | 113.5 (2) | C(17)—C(13)—C(14) | 102.0 (1) |

| | | | |
|---|---|---|---|
| C(10)—C(5)—C(4) | 111.9 (2) | C(18)—C(13)—C(12) | 110.9 (1) |
| C(10)—C(5)—C(6) | 112.1 (2) | C(18)—C(13)—C(14) | 112.0 (1) |
| C(7)—C(6)—C(5) | 110.0 (2) | C(18)—C(13)—C(17) | 111.6 (2) |
| C(8)—C(7)—C(6) | 112.1 (2) | C(13)—C(14)—C(8) | 113.9 (1) |
| C(9)—C(8)—C(7) | 110.9 (2) | C(15)—C(14)—C(8) | 119.5 (2) |
| C(14)—C(8)—C(7) | 111.4 (1) | C(15)—C(14)—C(13) | 102.9 (1) |
| C(14)—C(8)—C(9) | 107.9 (1) | C(16)—C(15)—C(14) | 104.4 (2) |
| C(10)—C(9)—C(8) | 114.0 (2) | C(17)—C(16)—C(15) | 107.9 (2) |
| C(11)—C(9)—C(8) | 111.1 (1) | C(20)—C(17)—C(13) | 117.9 (2) |
| C(11)—C(9)—C(10) | 112.9 (1) | C(20)—C(17)—C(16) | 112.1 (2) |
| C(5)—C(10)—C(1) | 107.8 (2) | C(21)—C(20)—C(17) | 114.2 (2) |
| C(9)—C(10)—C(1) | 109.5 (2) | C(22)—C(20)—C(17) | 110.0 (2) |
| C(9)—C(10)—C(5) | 106.1 (1) | C(22)—C(20)—C(21) | 109.8 (2) |
| C(19)—C(10)—C(1) | 110.0 (2) | O(1)—C(12)—C(11) | 121.2 (2) |
| C(19)—C(10)—C(5) | 112.3 (2) | O(1)—C(12)—C(13) | 124.4 (2) |
| C(19)—C(10)—C(9) | 111.1 (2) | | |

| | |
|---|---|
| C(1)—C(2)—C(3)—C(4) | 53.3 (2) |
| C(2)—C(3)—C(4)—C(5) | −55.2 (2) |
| C(3)—C(4)—C(5)—C(10) | 57.3 (2) |
| C(4)—C(5)—C(10)—C(1) | −55.5 (3) |
| C(5)—C(10)—C(1)—C(2) | 55.5 (2) |
| C(10)—C(1)—C(2)—C(3) | −55.2 (1) |
| C(5)—C(6)—C(7)—C(8) | 55.0 (4) |
| C(6)—C(7)—C(8)—C(9) | −51.6 (8) |
| C(7)—C(8)—C(9)—C(10) | 54.0 (5) |
| C(8)—C(9)—C(10)—C(5) | −56.1 (2) |
| C(9)—C(10)—C(5)—C(6) | 58.6 (4) |
| C(10)—C(5)—C(6)—C(7) | −60.1 (4) |
| C(8)—C(14)—C(13)—C(12) | −62.4 (5) |
| C(14)—C(13)—C(12)—C(11) | 60.0 (4) |
| C(13)—C(12)—C(11)—C(9) | −58.4 (2) |
| C(12)—C(11)—C(9)—C(8) | 53.4 (3) |
| C(11)—C(9)—C(8)—C(14) | −55.0 (4) |
| C(9)—C(8)—C(14)—C(13) | 62.2 (3) |
| C(13)—C(14)—C(15)—C(16) | −35.2 (11) |
| C(14)—C(15)—C(16)—C(17) | 12.3 (34) |
| C(15)—C(16)—C(17)—C(13) | 15.7 (35) |
| C(16)—C(17)—C(13)—C(14) | −36.7 (8) |
| C(17)—C(13)—C(14)—C(15) | 45.4 (8) |

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). Refinement was performed by *SHELX*76 (Sheldrick, 1976) using full-matrix least squares, with anisotropic thermal factors for all the non-H atoms, isotropic for H atoms. The H atoms were placed in calculated positions on the corresponding C atoms (C—H = 1.08 Å) and were not refined. Calculations were carried out on a VAX 3300. Geometrical calculations were performed with *XANADU* (Roberts & Sheldrick, 1975). Molecular illustrations were drawn with *FRODO* (Jones, 1978).

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71222 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1047]

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# 2-Amino-2-carboxyethylphosphinic Acid Monohydrate

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## Abstract

2-Amino-2-carboxyethylphosphinic acid exists as a zwitterion (2-ammonio-2-carboxyethylphosphinate) with anionic phosphinic, cationic alkylammonium and neutral carboxyl groups. The P—C—C—C and P—C—C—N conformations are *gauche* and *trans*, respectively. In contrast to 2-amino-2-carboxyethylphosphonic acid, intramolecular hydrogen bonding from ammonium to phosphinic moieties does not occur. Each phosphinic O atom accepts two intermolecular hydrogen bonds, as does the water molecule; every ammonium, carboxyl and water H atom participates.

## Comment

2-Amino-2-carboxyethylphosphinic acid [(1), 2-amino-3-(hydroxyphosphinyl)propionic acid, phosphinoalanine] has been isolated from fermentation broths of *Streptomyces hygroscopicus* (Seto, Imai, Tsuruoka, Ogawa, Satoh, Sasaki & Otake, 1983). As part of our continued interest in the biosynthesis and energetics of carbon-phosphorus bond formation (Seidel, Freeman, Seto & Knowles, 1988; Schwalbe & Freeman, 1990; Seidel, Freeman, Schwalbe & Knowles, 1990; Pollack, Freeman, Pompliano & Knowles, 1992) we have determined the crystal structure of (1), which was a key intermediate in the synthesis of the natural products phosphinopyruvate and carboxyphosphinopyruvate (Pollack *et al.*, 1992). The structurally related phosphonate analogues are antagonists of the NMDA receptor (Whitten, Harrison, Weintraub & McDonald, 1992).