

Table 3. Charge-density distribution calculated by the CNDO/2 method

Cl	-0.17	C(2)	-0.03
S	-0.45	C(3)	-0.11
N(1)	-0.17	C(4)	-0.01
N(2)	-0.11	C(5)	-0.03
N(3)	-0.15	C(6)	-0.05
C(1)	0.15	C(7)	0.27

factors like solubility, steric effects and so on also play critical roles in determining the activity of a particular compound, no specific comment about this can be made.

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References

- AGRAWAL, K. C., BOOTH, B. A. & SARTORELLI, A. C. (1968). *J. Med. Chem.* **11**, 701–703.
- AGRAWAL, K. C., CUSHLEY, R. J., McMURRAY, W. J. & SARTORELLI, A. C. (1970). *J. Med. Chem.* **13**, 431–434.
- CHATTOPADHYAY, D., BANERJEE, T., MAZUMDAR, S. K., GHOSH, S. & KURODA, R. (1987). *Acta Cryst.* **C43**, 974–977.
- CHATTOPADHYAY, D., MAZUMDAR, S. K., BANERJEE, T. & SHELDRIK, W. S. (1989). *Acta Cryst.* **C45**, 314–317.
- DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221–234.
- GHOSH, S., RAY, P. K., BANDYOPADHYAY, T. K. & GUHA, A. K. (1987). *Transition Met. Chem.* **12**, 219–222.
- KÁLMÁN, A., ARGAY, G. & CZUGLER, M. (1972). *Cryst. Struct. Commun.* **1**, 375–378.
- KIRSCHNER, S., WEI, Y. K., FRANCIS, D. & BERGMAN, J. G. (1966). *J. Med. Chem.* **9**, 369–372.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- NANDI, A. K., CHAUDHURI, S., MAZUMDAR, S. K. & GHOSH, S. (1984a). *J. Chem. Soc. Perkin Trans. 2*, pp. 1729–1733.
- NANDI, A. K., CHAUDHURI, S., MAZUMDAR, S. K. & GHOSH, S. (1984b). *Acta Cryst.* **B40**, 1193–1196.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd ed. Ithaca: Cornell Univ. Press.
- POPLE, J. A. & BEVERIDGE, D. L. (1970). *Approximate Molecular Orbital Theory*. New York: McGraw-Hill.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SORKIN, E., ROTH, W. & ERLMEYER, H. (1952). *Helv. Chim. Acta*, **36**, 1736–1741.
- TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5065–5070.

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Structure of (2R)-2-[(1S,2R,3S)-3-Hydroxy-2-methylcyclopentyl]-6-methyl-6-heptenoic Acid

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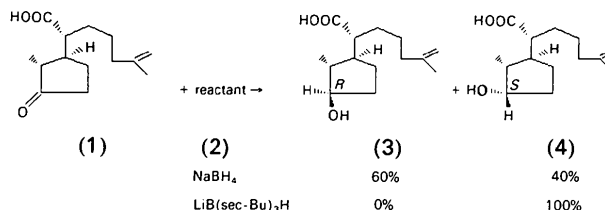
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Abstract. $C_{14}H_{24}O_3$, $M_r = 240.3$, triclinic, $P\bar{1}$, $a = 8.532$ (1), $b = 8.596$ (1), $c = 10.425$ (3) Å, $\alpha = 100.89$ (1), $\beta = 100.11$ (1), $\gamma = 104.18$ (2)°, $V = 707.9$ (5) Å³, $Z = 2$, $D_x = 1.127$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71070$ Å, $\mu = 0.053$ mm⁻¹, $F(000) = 264$, $T = 294$ K, $R = 0.049$, $wR = 0.053$ for 938 significant reflections. X-ray diffraction analysis clearly shows a *cis* stereochemistry for the title compound obtained when the reducing agent of the corresponding cyclopentanone is L-selectride.

Introduction. The stereochemistry of nucleophilic reagent addition on 2-alkyl- and 3-alkylcyclopentanones (Morrison & Mosher, 1971; Brown & Dickason, 1970; Richer & Belanger, 1966) showed that substituents in position 2 have a stronger influence on the addition stereochemistry than substituents

in position 3. In connection with a total synthesis of (1S,2S)-dihydroxycholecalciferol, J. Ficini & I. Daoust-Maleval (personal communication, not yet published) had to reduce the cyclopentanone (1). Reduction by sodium borohydride led to a mixture of both isomers (3) and (4), but the use of a more bulky reducing agent such as L-selectride [LiB(sec-Bu)₃H] was assumed, from NMR results, to lead to the *cis* isomer.



The resulting alcohol (4) is a key intermediate in the total synthesis and its structure had to be deduced without ambiguity; this is why its structure was solved by X-ray analysis.

Experimental. L-Selectride reduces cyclopentanone (1), in THF at 195 K. The resulting solution, slowly evaporated at room temperature, gives colourless bright crystals. Crystal: 0.2 × 0.3 × 0.1 mm; precession, P $\bar{1}$; Philips PW1100 diffractometer, graphite monochromator, Mo K α radiation; unit-cell parameters from least squares on 25 reflections, $8 < \theta < 14^\circ$, intensity measurements by θ - 2θ scan; $\sin\theta/\lambda$ range 0.05–0.52 Å⁻¹; scan speed 0.06° s⁻¹; background measured for half of scan time, before and after every scan; scan range (1.0 + 0.345tan θ)°; two standard reflections measured every 2 h, negligible variation; four octants measured, hkl , $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$; 1587 independent reflections collected and 938 reflections considered observed [$I > 3\sigma(I)$]; computing program: CRYSTALS (Watkin, Carruthers & Betteridge, 1985); structure solved with MULTAN84 (Main, Germain & Woolfson, 1984); refinement on F ; calculations performed on MicroVAX II; scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); H atoms located on difference maps and put in fixed positions with a variable overall isotropic thermal parameter; absorption corrections were not applied; secondary absorption not observed; weighting scheme $w = 1$; average shift/e.s.d. = 0.02 in the last cycle; $N_{\text{ref}}/N_{\text{var par}} = 6$; $R(F) = 0.049$, $wR(F) = 0.053$; $S = 1.12$; max. height in final difference Fourier synthesis 0.15 e Å⁻³.

Table 1 gives the atomic parameters and Table 2 selected interatomic distances and bond angles.*

Discussion. The unit cell contains two C₁₄H₂₄O₃ entities (Fig. 1). It can be seen that C(18) and O(1) bound to C(13) and C(14) are respectively on the same side of the five-membered ring and on the opposite side with respect to H(131) and H(141) bound to C(13) and C(14); distances to the C(13)C(14)C(15)C(16)C(17) mean plane are C(18) – 0.344, O(1) – 1.621, H(131) 1.343, H(141) 0.349 Å. This structure corresponds to the *cis* isomer (4), which confirms NMR results. Additionally, it can be noted that the ring conformation is not very far from a 'symmetrical envelope' with the following torsion angles: C(13)C(14)C(15) – 26.6, C(14)C(15)C(16) 4.5, C(15)C(16)C(17) 18.6, C(16)C(17)C(13) – 35.2,

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53096 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters with e.s.d.'s in parentheses

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq} (Å ²)
O(1)	0.3466 (4)	0.4754 (5)	0.8577 (4)	0.0563
O(2)	–0.3283 (4)	0.5909 (5)	0.8306 (4)	0.0595
O(3)	–0.1571 (4)	0.7172 (5)	1.0289 (4)	0.0609
C(13)	0.2201 (7)	0.6849 (8)	0.7903 (6)	0.0601
C(14)	0.2668 (7)	0.5293 (9)	0.7468 (6)	0.0591
C(15)	0.1006 (7)	0.3989 (8)	0.6746 (6)	0.0712
C(16)	–0.0310 (7)	0.4566 (7)	0.7355 (6)	0.0643
C(17)	0.0561 (6)	0.6257 (7)	0.8337 (5)	0.0444
C(18)	0.3536 (8)	0.8156 (9)	0.8997 (9)	0.0881
C(20)	–0.0498 (6)	0.7480 (7)	0.8379 (5)	0.0454
C(21)	–0.1957 (7)	0.6778 (7)	0.8974 (6)	0.0470
C(22)	–0.1061 (6)	0.7915 (7)	0.7065 (6)	0.0536
C(23)	–0.1917 (7)	0.9281 (7)	0.7163 (6)	0.0620
C(24)	–0.2359 (7)	0.9752 (7)	0.5837 (7)	0.0677
C(25)	–0.3689 (7)	0.8546 (7)	0.4751 (6)	0.0540
C(26)	–0.4711 (8)	0.7224 (9)	0.4908 (7)	0.0771
C(27)	–0.3866 (9)	0.897 (1)	0.3422 (8)	0.0945

Table 2. Main interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses

O(1)–C(14)	1.448 (6)	O(2)–C(21)	1.198 (6)
O(3)–C(21)	1.310 (6)	C(13)–C(14)	1.499 (8)
C(13)–C(17)	1.543 (7)	C(13)–C(18)	1.515 (9)
C(14)–C(15)	1.537 (8)	C(15)–C(16)	1.521 (8)
C(16)–C(17)	1.534 (7)	C(17)–C(20)	1.545 (7)
C(20)–C(21)	1.530 (7)	C(20)–C(22)	1.516 (7)
C(22)–C(23)	1.525 (8)	C(23)–C(24)	1.523 (8)
C(24)–C(25)	1.474 (8)	C(25)–C(26)	1.309 (8)
C(25)–C(27)	1.492 (9)		
C(17)–C(13)–C(14)	104.0 (5)	C(18)–C(13)–C(14)	113.5 (5)
C(18)–C(13)–C(17)	113.2 (5)	C(13)–C(14)–O(1)	113.4 (5)
C(15)–C(14)–O(1)	109.2 (5)	C(15)–C(14)–C(13)	104.4 (5)
C(16)–C(15)–C(14)	105.8 (5)	C(16)–C(17)–C(13)	103.7 (5)
C(20)–C(17)–C(13)	114.6 (5)	C(20)–C(17)–C(16)	114.2 (4)
C(21)–C(20)–C(17)	107.1 (4)	C(22)–C(20)–C(17)	116.0 (4)
C(22)–C(20)–C(21)	112.3 (4)	O(3)–C(21)–O(2)	123.9 (5)
C(20)–C(21)–O(2)	123.5 (5)	C(20)–C(21)–O(3)	112.6 (5)
C(23)–C(22)–C(20)	115.2 (5)	C(24)–C(23)–C(22)	113.3 (5)
C(25)–C(24)–C(23)	118.1 (5)	C(26)–C(25)–C(24)	124.5 (6)
C(27)–C(25)–C(24)	114.8 (6)	C(27)–C(25)–C(26)	120.6 (6)

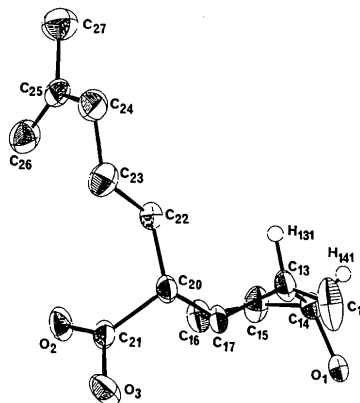


Fig. 1. ORTEP (Johnson, 1976) view of the structure.

C(17)C(13)C(14) 38.3°. Molecules are connected by intermolecular hydrogen bonds; the first is between O(1) of one molecule and O(2) of a second molecule [O(1)—O(2) = 2.792 Å] with O(1)H(1)O(2) = 166°; the second is between O(1) of the first molecule and O(3) of a third molecule [O(1)—O(3) = 2.617 Å] with O(1)H(3)O(3) = 173°.

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† Deceased.

References

- BROWN, H. C. & DICKASON, W. C. (1970). *J. Am. Chem. Soc.* **92**, 709–710.
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 MAIN, P., GERMAIN, G. & WOOLFSON, M. M. (1984). *MULTAN84. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 MORRISON, J. D. & MOSHER, H. S. (1971). *Asymmetric Organic Reactions*, p. 117. Englewood Cliffs: Prentice-Hall.
 RICHER, J. C. & BELANGER, P. (1966). *Can. J. Chem.* **44**, 2057–2066.
 WATKIN, D. J., CARRUTHERS, J. R. & BETTERIDGE, D. W. (1985). *CRYSTALS*. Chemical Crystallography Laboratory, Univ. of Oxford, England.

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Structure du Propanediammonium-1,3 Monohydrogénomonophosphate Monohydrate

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Abstract. $C_3H_{12}N_2^+ \cdot HPO_4^{2-} \cdot H_2O$, $M_r = 190.14$, monoclinic, $P2_1/c$, $a = 6.956$ (2), $b = 16.654$ (3), $c = 7.782$ (1) Å, $\beta = 113.80$ (1)°, $V = 824.8$ (6) Å³, $Z = 4$, $D_m = 1.544$, $D_x = 1.531$ Mg m⁻³, $\lambda(\text{Ag } K\alpha) = 0.5608$ Å, $\mu = 1.647$ mm⁻¹, $F(000) = 408$, $T = 298$ K. The structure was solved by the Patterson method and refined to a final R value of 0.049 for 1764 observed independent reflections. The acidic phosphoric groups are connected through O—H...O hydrogen bonds, so that infinite chains parallel to the c axis with anionic period $[H_2P_2O_8(H_2O)]^{4-}$ are formed in the structure. The chains are themselves interconnected by means of N—H...O hydrogen bonds originating from the $[NH_3(CH_2)_3NH_3]^{2+}$ cation so as to build a three-dimensional network.

Introduction. L'étude de $NH_3(CH_2)_3NH_3 \cdot HPO_4 \cdot H_2O$ s'inscrit dans le cadre d'une étude systématique de l'interaction de l'acide monophosphorique H_3PO_4 avec les diamines aliphatiques à chaînes linéaires répondant à la formule chimique $NH_2(CH_2)_nNH_2$ où $n > 1$. Plusieurs structures de complexes de l'éthylènediamine ($n = 2$) ont été établies: Na_2-

$NH_3(CH_2)_2NH_3 \cdot (HPO_4)_2 \cdot 6H_2O$ (Averbuch-Pouchot, Durif & Guitel, 1987), $NH_3(CH_2)_2NH_3 \cdot HPO_4$ (Averbuch-Pouchot & Durif, 1987), $NH_3(CH_2)_2NH_3 \cdot 2H_2PO_4$ (Kamoun, Jouini & Daoud, 1989) et $NH_3(CH_2)_2NH_3 \cdot 2H_2PO_4 \cdot H_3PO_4$ (Bagieu-Beucher, Durif & Guitel, 1989).

Dans le présent travail, nous décrivons la structure cristalline de ce nouveau complexe de monophosphate, dont la préparation, l'analyse et les caractéristiques cristallographiques ont été signalées (Kamoun, Jouini & Daoud, 1990).

Partie expérimentale. Cristal parallélépipédique, dimensions: 0,12 × 0,09 × 0,014 mm; D_m par pycnométrie (bromobenzène); Philips PW1100; monochromateur: graphite; paramètres cristallins obtenus avec 25 réflexions ($11 < \theta < 13^\circ$); domaine des mesures: 3 à 30° (θ); type de balayage: ω ; domaine de balayage (1,2 + 0,2 tg θ)°; vitesse de balayage 0,03 s⁻¹; réflexions de référence: 241, 241, 133; variation négligeable; temps de mesure du fond continu fixé à 10 s; nombre de réflexions mesurées: 1854 ($\pm h, k, l$); $h_{\max} = 10$; $k_{\max} = 26$; $l_{\max} = 11$; correction