References

ATAL, C. K., KAPUR, K. K., CULVENOR, C. C. J. & SMITH, L. W. (1966). *Tetrahedron Lett.* pp. 537–544.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

CULVENOR, C. C. J. & SMITH, L. W. (1972). *An. R. Soc. Esp. Fís. Quím.* **68**, 883–892.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MACKAY, M. F. & CULVENOR, C. C. J. (1982). *Acta Cryst.* B**38**, 2754–2758.

MACKAY, M. F., SADEK, M. & CULVENOR, C. C. J. (1984). *Acta Cryst.* C**40**, 1073–1077.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

YADAV, V. K., RÜEGER, H. & BENN, M. H. (1984). *Heterocycles*, **22**, 2735–2738.

Acta Cryst. (1985). C**41**, 1477–1480

13,14-Didehydro-11-deoxy-15-ketoprostaglandin E_1 (at 173 K), $C_{20}H_{30}O_4$

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(*Received* 23 *February* 1985; *accepted* 10 *June* 1985)

Abstract. $M_r = 334{\cdot}5$, monoclinic, $P2_1/n$, $a = 5{\cdot}544$ (1), $b = 12{\cdot}834$ (2), $c = 27{\cdot}587$ (6) Å, $\beta = 92{\cdot}22$ (2)°, $V = 1961{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}13$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}72$ cm^{-1}, $F(000) = 728$, final $R = 0{\cdot}061$ for 2463 unique reflections above background [$I > 2\sigma(I)$]. The molecule does not have the hairpin conformation that is characteristic of most prostaglandin molecules. Instead, an 'L'-shaped conformation is revealed that is similar to the structure of prostaglandin B_1. The alkyl chains have the fully extended all-*trans* conformation. The five-atom ring has an envelope conformation. The stereochemical features of the title compound are compared with those of prostaglandin E_1 and two other prostaglandin E_1 analogs.

Introduction. The synthesis of the title compound (hereinafter referred to as 7ME1) will be reported separately (Matthews, 1985). Naturally occurring and synthetic prostaglandins* tend to have a hairpin conformation in the solid state. In this conformation the two side chains are approximately parallel. The single reported exception to that generalization is PGB_1 (DeTitta, Langs & Edmonds, 1979), whose crystal structure reveals an 'L' conformation in which the side chains are approximately perpendicular to each other. The crystal structure of a 13-dehydroprostaglandin E_1 analog (Oliver & Strickland, 1983), the only published report of an alkyne-containing prostaglandin structure, revealed a relatively planar hairpin-shaped molecule. The structural analysis of 7ME1 was undertaken in order to determine the conformation of this related molecule in the solid state.

Experimental. Crystals of the compound obtained from Dr R. S. Matthews of these laboratories, seed crystals obtained as a waxy residue from long-term (~1 year) storage of the compound, crystallized by slow evaporation of a diethyl ether–ethyl acetate solution; clear needle-shaped crystal, $0{\cdot}06 \times 0{\cdot}13 \times 0{\cdot}25$ mm, mounted on glass fiber, Syntex $P2_1$ autodiffractometer, data crystal continuously bathed in cold dry nitrogen gas stream maintained at 173 K using a Syntex LT-1 low-temperature attachment, Laue symmetry $2/m$ with systematic absences $0k0$ for k odd and $h0l$ for $h+l$ odd; lattice parameters by least-squares refinement of 23 carefully centered reflections, Miller indexes for data collection $h = 0$ to 6, $k = 0$ to 15, $l = -32$ to 32 using $\theta/2\theta$ scan with variable scan rate of 4·0 to 29·3° min^{-1}; intensities of 4 check reflections (200, 040, 004, $\bar{2}\bar{2}\bar{2}$) monitored every 100 reflections revealed only random variations (<6%) from mean intensities; 3556 unique reflections ($2{\cdot}0 < 2\theta < 50°$), 2463 with $I > 2\sigma(I)$ used in solution and refinement of structure, data corrected for Lorentz and polarization effects, not for absorption;

* Abbreviations employed: PG, prostaglandin; PGE_1, (11*R*,13*E*,15*S*)-11,15-dihydroxy-9-oxoprost-13-en-1-oic acid; PGB_1, (13*E*,15*S*)-15-hydroxy-9-oxoprosta-8(12),13-dien-1-oic acid; CE1S, (15*S*)-15-hydroxy-7-oxa-9-oxoprost-13-yn-1-oic acid; 7ME1,9,15-dioxoprost-13-yn-1-oic acid.

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Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for the non*-H *atoms of* 7ME1

	x	*y*	*z*	*U**
O(1)	12615 (4)	9255 (2)	93 (1)	45 (1)
O(2)	14142 (4)	10497 (2)	580 (1)	50 (1)
O(3)	−1380 (4)	4998 (2)	1604 (1)	42 (1)
O(4)	10131 (4)	7695 (2)	2822 (1)	56 (1)
C(1)	12586 (5)	9748 (3)	468 (1)	35 (1)
C(2)	10809 (6)	9566 (3)	855 (1)	42 (1)
C(3)	9189 (5)	8631 (3)	771 (1)	37 (1)
C(4)	7643 (5)	8400 (3)	1202 (1)	37 (1)
C(5)	5991 (5)	7465 (2)	1128 (1)	33 (1)
C(6)	4693 (5)	7174 (2)	1584 (1)	34 (1)
C(7)	3100 (5)	6213 (2)	1528 (1)	31 (1)
C(8)	2074 (5)	5839 (2)	1999 (1)	28 (1)
C(9)	84 (5)	5025 (2)	1938 (1)	30 (1)
C(10)	279 (5)	4254 (2)	2350 (1)	34 (1)
C(11)	2199 (5)	4683 (2)	2699 (1)	33 (1)
C(12)	3836 (5)	5317 (2)	2372 (1)	29 (1)
C(13)	5510 (5)	6007 (2)	2637 (1)	29 (1)
C(14)	6923 (5)	6550 (2)	2851 (1)	33 (1)
C(15)	8705 (5)	7257 (2)	3073 (1)	35 (1)
C(16)	8601 (8)	7437 (3)	3607 (2)	60 (1)
C(17)	10687 (8)	8021 (3)	3826 (2)	75 (2)
C(18)	10631 (14)	8265 (5)	4342 (2)	127 (3)
C(19)	12811 (21)	8778 (7)	4575 (3)	215 (5)
C(20)	13083 (27)	8900 (10)	5007 (4)	296 (9)

* Equivalent isotropic U is defined as 1/3 trace (U_{ij}).

standard deviations of observed structure factor amplitudes based solely on counting statistics. Structure solved by direct methods and refined using *SHELXTL* (Sheldrick, 1984); H atoms were included and refined from their $\Delta\rho$ locations, those of C(20) could not be located; least-squares refinement on F yielded $R = 0{\cdot}061$, $wR = 0{\cdot}059$, $w = \sigma^{-2}(|F_o|)$, $S = 1{\cdot}12$, mean and max. Δ/σ in final refinement cycle 0·028 and 0·138, respectively; atomic scattering factors from Ibers & Hamilton (1974); final difference electron density map revealed featureless background below $\pm 0{\cdot}4$ e $Å^{-3}$, except for diffuse peaks below $\pm 0{\cdot}7$ e $Å^{-3}$ in vicinity of H-atom locations on C(20).

Discussion. The final atomic parameters for 7ME1 are given in Table 1.* A perspective drawing of 7ME1 is shown in Fig. 1, which also illustrates the atom-labeling scheme. A stereoscopic view of the molecular packing is shown in Fig. 2. Bond lengths, bond angles and torsion angles are given in Table 2.

The 'L'-shaped conformation of 7ME1 is unusual and has been observed in only one other prostaglandin crystal structure, PGB_1 (DeTitta, Langs & Edmonds, 1979), where the 'L'-shaped conformation was rationalized as the consequence of the all-*trans* conjugated dienone residue, O(9)=C(9)–C(8)=C(12)–C(13)=C(14)–C(15), and the *cis* orientation of the O(15) hydroxyl group to the C(13)=C(14) bond [possibly due to the strong intermolecular H bonding involving O(5)]. Since 7ME1 lacks the unsaturation at the C(8)–C(12) bond and has no H bonding involving the ketone function at C(15) (*cf.* Fig. 2), similar logic cannot be used to rationalize the 'L'-shaped conformation of 7ME1. The 'L' shape of 7ME1 may be an intrinsic structural feature of the molecule.

The conformations of the side chains of four E_1 analog prostanoid molecules, 7ME1, PGE_1 (Spek, 1977), PGB_1 (DeTitta, *et al.*, 1979) and 11-deoxy-7-oxa-13,14-didehydroprostaglandin E_1 (hereinafter referred to as CE1S) (Oliver & Strickland, 1983), are compared in Fig. 3. The figure reveals two topologies of the upper (α) chains, with 7ME1 and PGE_1, and PGB_1 and CE1S being similar. The figure also shows that the topologies of the bottom (ω) chains of the 'L'-shaped

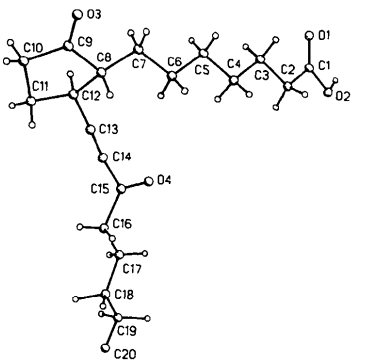

Fig. 1. Perspective illustration of 7ME1.

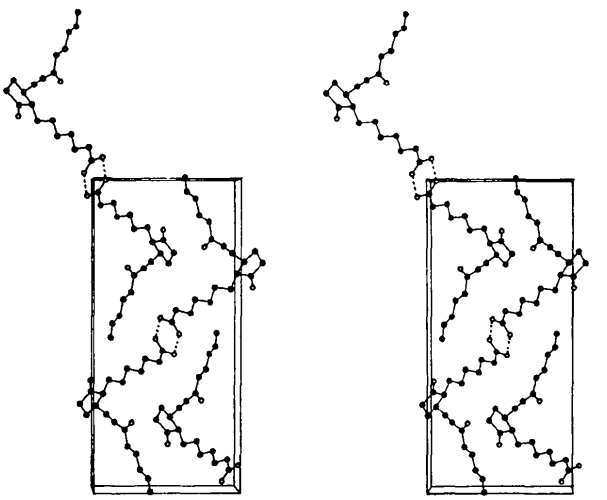

Fig. 2. Stereoview of the molecular packing of 7ME1 as viewed parallel to the *a* axis.

* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters and torsion angles for 7ME1 and CE1S have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42262 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecules, 7ME1 and PGB_1, are similar, but that the bottom chains of the hairpin molecules, PGE_1 and CE1S, have different topologies. These trends in side-chain conformations of these analogs of PGE_1 suggest these prostanoid molecules possess common low-energy regions of conformational energy space that may be important in determining biological activities. It is not apparent whether chemical or crystallographic influences determine which conformational motif will be adopted by a given E_1 analog.

A comparison of the torsion angles of the backbone of the non-H atoms of the 13-14-didehydroprostaglandin E_1 analogs CE1S and 7ME1 (listed in the supplementary material) reveals an interesting feature.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *for 7ME1*

O(1)–C(1)	1·215 (4)	O(2)–C(1)	1·320 (4)
O(3)–C(9)	1·206 (4)	O(4)–C(15)	1·210 (4)
C(1)–C(2)	1·499 (4)	C(2)–C(3)	1·511 (5)
C(3)–C(4)	1·521 (4)	C(4)–C(5)	1·519 (4)
C(5)–C(6)	1·520 (4)	C(6)–C(7)	1·521 (4)
C(7)–C(8)	1·515 (4)	C(8)–C(9)	1·523 (4)
C(8)–C(12)	1·545 (4)	C(9)–C(10)	1·507 (4)
C(10)–C(11)	1·512 (4)	C(11)–C(12)	1·538 (4)
C(12)–C(13)	1·458 (4)	C(13)–C(14)	1·188 (4)
C(14)–C(15)	1·460 (4)	C(15)–C(16)	1·494 (5)
C(16)–C(17)	1·487 (6)	C(17)–C(18)	1·457 (7)
C(18)–C(19)	1·499 (12)	C(19)–C(20)	1·208 (13)
O(1)–C(1)–O(2)	123·2 (3)	O(1)–C(1)–C(2)	123·9 (3)
O(2)–C(1)–C(2)	112·9 (3)	C(1)–C(2)–C(3)	114·7 (3)
C(2)–C(3)–C(4)	112·6 (3)	C(3)–C(4)–C(5)	113·8 (3)
C(4)–C(5)–C(6)	112·7 (3)	C(5)–C(6)–C(7)	114·0 (3)
C(6)–C(7)–C(8)	113·9 (2)	C(7)–C(8)–C(9)	114·7 (2)
C(7)–C(8)–C(12)	117·4 (2)	C(9)–C(8)–C(12)	102·3 (2)
O(3)–C(9)–C(8)	124·6 (3)	O(3)–C(9)–C(10)	125·7 (3)
C(8)–C(9)–C(10)	109·7 (2)	C(9)–C(10)–C(11)	105·7 (2)
C(10)–C(11)–C(12)	103·6 (2)	C(8)–C(12)–C(11)	104·4 (2)
C(8)–C(12)–C(13)	116·4 (2)	C(11)–C(12)–C(13)	113·9 (2)
C(12)–C(13)–C(14)	178·2 (3)	C(13)–C(14)–C(15)	175·1 (3)
O(4)–C(15)–C(14)	119·6 (3)	O(4)–C(15)–C(16)	123·0 (3)
C(14)–C(15)–C(16)	117·4 (3)	C(15)–C(16)–C(17)	114·8 (3)
C(16)–C(17)–C(18)	117·4 (5)	C(17)–C(18)–C(19)	117·7 (6)
C(18)–C(19)–C(20)	123·3 (11)		
O(2)–C(1)–C(2)–C(3)	−172·9 (3)		
C(1)–C(2)–C(3)–C(4)	172·8 (3)		
C(2)–C(3)–C(4)–C(5)	179·9 (3)		
C(3)–C(4)–C(5)–C(6)	173·1 (3)		
C(4)–C(5)–C(6)–C(7)	−177·7 (2)		
C(5)–C(6)–C(7)–C(8)	172·3 (2)		
C(6)–C(7)–C(8)–C(9)	168·9 (2)		
C(7)–C(8)–C(9)–C(10)	144·3 (2)		
C(7)–C(8)–C(12)–C(13)	73·9 (3)		
C(8)–C(9)–C(10)–C(11)	7·3 (3)		
C(9)–C(10)–C(11)–C(12)	−28·0 (3)		
C(10)–C(11)–C(12)–C(13)	166·5 (2)		
C(11)–C(12)–C(13)–C(14)	102·6 (103)*		
C(12)–C(13)–C(14)–C(15)	87·8 (109)*		
C(13)–C(14)–C(15)–C(16)	161·6 (35)		
C(14)–C(15)–C(16)–C(17)	170·5 (3)		
C(15)–C(16)–C(17)–C(18)	177·1 (4)		
C(16)–C(17)–C(18)–C(19)	175·2 (6)		
C(17)–C(18)–C(19)–C(20)	−170·8 (10)		

* E.s.d.'s are large because of the formally linear C(13)–C(14) bond.

The molecules differ in conformation about the 7–8, 14–15 and 15–16 bonds. Thus, rotations of −92·3, 180 and −109·0° about the C(7)–C(8), C(14)–C(15) and C(15)–C(16) bonds, respectively, of 7ME1 produce a conformer that is superimposable on the solid-state conformer of CE1S.

The five-atom ring of 7ME1 adopts a C(12) envelope conformation. In this conformation the atoms C(8), C(9), C(10), C(11) and O(3) are approximately coplanar. Similar C(12) envelope conformations have been observed for CE1S, PGE_1, PGE_2 and $PGF_{2\beta}$ (DeTitta, Langs, Edmonds & Duax, 1980).

The ring/chain junction geometry (*cf.* Oliver & Strickland, 1983, for a tabulation of these metrical features) is another important conformational descriptor for PG molecules. The torsion angles of 7ME1 that define the ring/α-chain junction are Ω[C(6)–C(7)–C(8)–C(12)] = −71·9 (3)° and Ω[C(6)–C(7)–C(8)–C(9)] = 168·0 (2)°. This geometry is very similar to those of PGE_1 and PGA_1 in both the monoclinic (DeTitta *et al.*, 1979) and orthorhombic (Edmonds & Duax, 1975) forms. The incorporation of the alkyne functional group of 7ME1 precludes a quantitative evaluation of the ring/ω-chain torsion angles.

The 7ME1 molecule is relatively planar, although not quite as planar as the other 13,14-didehydroprostaglandin E_1 analog, CE1S. For 7ME1, the maximum displacements of any non-H atom from the least-squares plane defined by the 24 non-H atoms are 0·79 (1) [O(1)] and −0·68 (1) Å [O(3)]. Each alkyl chain is almost perfectly planar. The C atoms of the α chain, C(1) through C(7), reside within ±0·13 (1) Å of their common plane. The C atoms of the saturated portion of the ω chain, C(15) through C(20), are located within ±0·07 (1) Å of their common plane. The dihedral angle between these two planes is 27·6 (8)°.

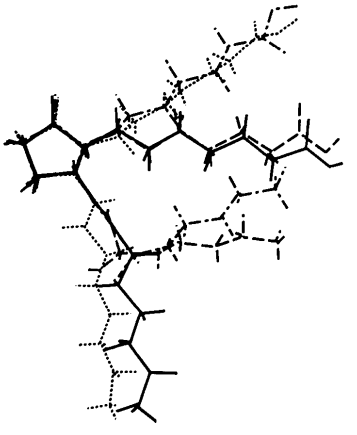

Fig. 3. Illustration of the side-chain conformations of four PGE_1 analog molecules. The five-membered rings have been superimposed. The representations of the molecules are 7ME1, solid line; CE1S, dash-dotted line; PGE_1, dashed line; and PGB_1, dotted line.

The planar residues of the α and ω chains form dihedral angles of 52·3 (6) and 44·0 (8)°, respectively, with the basal plane of the five-membered ring [defined by the non-H atoms C(8) through C(11)].

The bond lengths, bond angles and thermal parameters for the atoms of the α chain, the five-atom ring and the unsaturated portion of the ω chain show no unusual features. However, the thermal parameters and the bond lengths for the terminal *n*-pentyl segment of the ω chain display significant effects of high thermal motion (even at 173 K). The magnitude and direction of the thermal ellipsoids of atoms C(16) through C(20) are consistent with either static or dynamic torsional disorder about the C(14)—C(15) bond. Owing to this high thermal motion, the H atoms of the terminal C atom, C(20), of the ω chain were not located and the C(19)—C(20) bond length is foreshortened to 1·208 (13) Å.

The stereoscopic view shown in Fig. 2 reveals that the molecular packing is dominated by strong H bonds between the carboxyl groups of adjacent molecules. The pertinent contact distances are H(2)···O′(1) = 1·93 (5) and O(1)···O′(2) = 2·652 (4) Å. The oxygen atoms of the two ketone residues are not involved in H bonds. This H-bonding pattern is consistent with the fact that the 7ME1 molecule has a deficiency of H-bond donors (the carboxylic OH group) relative to H-bond acceptors (the three carbonyl O atoms). The natural prostaglandin molecules have a better balance of H-bond donor and acceptor groups by having two or three alcoholic hydroxyl groups that can function simultaneously as H-bond donors and acceptors and frequently participate in bifurcated H bonds.

References

DeTitta, G. T., Langs, D. A. & Edmonds, J. W. (1979). *Biochemistry*, **18**, 3387–3391.

DeTitta, G. T., Langs, D. A., Edmonds, J. W. & Duax, W. L. (1980). *Acta Cryst.* B**36**, 638–645.

Edmonds, J. W. & Duax, W. L. (1975). *J. Am. Chem. Soc.* **97**, 413–417.

Ibers, J. A. & Hamilton, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 72–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Matthews, R. S. (1985). In preparation.

Oliver, J. D. & Strickland, L. C. (1983). *Acta Cryst.* C**39**, 380–383.

Sheldrick, G. M. (1984). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Nicolet XRD Division, Madison, WI.

Spek, A. L. (1977). *Acta Cryst.* B**33**, 816–824.

Acta Cryst. (1985). C**41**, 1480–1482

Structure of 2-Methyl-6-(4-methyl-2-oxo-3-cyclohexen-1-yl)hept-2-enoic Acid, a Natural 1-Bisabolone

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(*Received* 3 *April* 1985; *accepted* 20 *June* 1985)

Abstract. $C_{15}H_{22}O_3$, $M_r = 250·34$, orthorhombic, $P2_12_12_1$, $a = 8·109$ (3), $b = 11·806$ (4), $c = 15·132$ (4) Å, $U = 1448·7$ (8) Å^3, $Z = 4$, $D_x = 1·148$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·08$ mm^{-1}, $F(000) = 544$, $T = 294$ (1) K, final $R = 0·055$ for 899 unique diffractometer data and 164 refined parameters. The relative configuration of a natural 1-bisabolone is shown to be 6*R*,7*S*. In the crystal the molecules are linked by H bonds to form chains parallel to **b** [O···O 2·709 (4), H···O 1·760 (3) Å, ∠C—O—H 115·1 (4)°].

Introduction. During the last decade an increasing number of sesquiterpenoids, representing the skeleton of 1-bisabolone (1), have been isolated from various plant sources, mainly by F. Bohlmann. Among these are (1), itself, from *Stevia purpurea* Pers. (Bohlmann, Zdero & Schöneweiss, 1976), (2) from *Ptilostemon chamaepeuce* Less. (Bohlmann, Rao & Schwarz, 1974), (3) from *Stevia ovata* Willd. (Bohlmann, Suwita, Natu, Czerson

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