We thank Professor E. Vogel for a gift of a sample of the substance.

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Acta Cryst. (1983). C**39**, 380–383

11-Deoxy-7-oxa-13,14-didehydroprostaglandin E_1* (at 173 K), $C_{19}H_{30}O_5$

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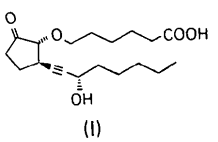
Abstract. $M_r = 338{\cdot}4$, monoclinic, $P2_1$, $a = 10{\cdot}785$ (3), $b = 6{\cdot}841$ (2), $c = 13{\cdot}176$ (4) Å, $\beta = 103{\cdot}05$ (2)°, $V = 947{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}19$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}079$ mm^{-1}. Final $R = 0{\cdot}054$ for 1094 unique reflections. The molecule is virtually coplanar and possesses the 'hairpin' conformation characteristic of prostaglandin molecules. The side chains are in the fully extended all-*trans* conformation. A detailed comparison of the stereochemical features of the title compound and published prostaglandin structures is presented.

Introduction. The stereoselective syntheses of a series of 11-deoxy-7-oxa-prostaglandin analogs were recently accomplished (Matthews, Mihelich & McGowan, 1982). In the course of that work, the mixture of stereoisomers shown below was prepared. One of the two isomers crystallized and was thus obtained optically pure.



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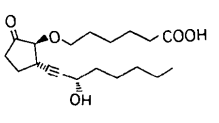

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For both compounds, the absolute stereochemistry at C(15) was known to be *S* [because the synthesis started with optically pure (*S*)-1-octyn-3-ol]. The relative stereochemistry at the ring junction [C(8) *vs* C(12)] was also known to be *trans*. However, in the absence of a crystal structure, it was impossible to tell which of the two structures represented the crystalline isomer. Solution of the structure defines the molecule's stereochemistry to be (I) and allows the absolute stereochemistry of a series of compounds to be assigned through comparative chemical procedures.

Experimental. Crystals of title compound (hereinafter referred to as CE1S) obtained from Dr R. S. Matthews, crystallized by slow evaporation of a hexane solution; clear, tablet-shaped crystal, 0·03 × 0·13 × 0·55 mm, mounted on a glass fiber, transferred to a 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 0*k*0 for *k* odd; solution and refinement of structure confirm space group to be $P2_1$, lattice parameters obtained by least-squares analysis of 14 carefully centered reflections, $hk\pm l$ quadrant of intensity data collected by θ–2θ scan technique with a variable scan rate of 4·0 to 29·3° min^{-1}, intensities of four check reflections (004,040,100,111) monitored every 100 reflections and revealed only a random variation (<2%) from their mean intensities; 1464 total reflections ($2{\cdot}5 < 2\theta < 45°$), 1377 unique reflections obtained after merging equivalent reflections ($R_{int} = 0{\cdot}045$), 1094 with $|F_o| \geq 3\sigma(|F_o|)$ used in solution and refinement of structure, data corrected for Lorentz and polarization

* Prostaglandin E_1 is (11α,13*E*,15*S*)-11,15-dihydroxy-9-oxo-prost-13-en-1-oic acid.

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effects; due to the small value of μ no absorption correction was necessary; standard deviations of observed structure-factor amplitudes calculated based solely on counting statistics.

The structure was solved by direct methods and refined using *SHELXTL* (Sheldrick, 1979). Examination of E maps revealed only a planar net of crosslinked triangles. Using a procedure described by DeTitta, Langs, Edmonds & Duax (1980), an eight-atom fragment of an all-*trans* planar zigzag chain was identified. The coordinates were then translated so that the local inversion center of the fragment was at the origin of the unit cell. Reiterative expansion and tangent refinement of these phases in space group $P1$ yielded the locations of all the non-H atoms of both molecules in the unit cell. The complete molecule was then shifted so that the structure conformed to the crystallographic symmetry and refinement was subsequently performed in space group $P2_1$. The enantiomorph chosen had the correct (S) absolute configuration for the octynol substituent.

During isotropic refinement of structure 020 was found to suffer from extinction ($\Delta F = -72$e) and eliminated; after convergence of least-squares refinement (on F) using anisotropic thermal parameters for non-H atoms difference density map was calculated and revealed locations of 30 H atoms of the molecule; to maintain ratio of observations: parameters at a reasonable value (4·55) methylene H atoms were included at their fixed, idealized positions [d(C—H) = 0·96 Å and <(H—C—H) = 109·5°] with their isotropic thermal parameters fixed at ~1·3 times equivalent isotropic thermal parameter of atom to which they are bonded; remaining hydroxyl, methine and methyl H-atom parameters refined using isotropic thermal parameters; least-squares refinement of this model yielded R = 0·054, wR = 0·060, S = 1·16, $F(000)$ = 368; in final refinement cycle mean and maximum shift:σ values 0·02 and −0·12 respectively; atomic scattering factors taken from Ibers & Hamilton (1974), weighting function w calculated according to $w^{-1} = \sigma^2(|F_o|) + p|F|^2$ where $\sigma(|F_o|)$ is the standard deviation of the structure factor and p is the ignorance factor (0·0012 in this work); final difference electron density map revealed a featureless background below 0·25e Å^{-3}.

Discussion. The final atomic parameters are given in Table 1.*

A perspective drawing of CE1S is shown in Fig. 1, which also illustrates the atom-labeling scheme used. The H atoms are labeled according to the atom to which they are bonded. Thus the H atom(s) bonded to atom n is labeled Hn (or Hna, Hnb, *etc.*). Bond lengths and bond angles are given in Table 2. The synthesis of the compound requires S absolute configuration at C(15). This knowledge allows assignment of absolute configuration at C(8) (R) and C(12) (R). The absolute stereochemistry of CE1S matches that of the naturally occurring prostaglandins.

The molecule is relatively planar with the maximum displacements of 0·49 Å [C(10)] and −0·55 Å [O(2)] from the best-fit plane defined by the 24 non-H atoms. Each alkyl chain is almost perfectly planar. The C atoms of the α chain, C(1) through C(6), are located within ± 0·05 Å of their common plane. Likewise the C atoms of the ω chain, C(15) through C(20), reside within ± 0·04 Å of their common plane. Since the dihedral angle between these two planes is only 6·9°, the two alkyl chains are virtually coplanar. Similar coplanarity of the alkyl chains has not been observed in other prostaglandin structures. This planarity is the

Table 1. *Atom coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *for the non*-H *atoms*

	x	y	z	U_{eq}*
C(1)	10509 (4)	5000	8494 (3)	34 (2)
C(2)	10462 (4)	5594 (11)	7395 (3)	39 (2)
C(3)	9314 (4)	4874 (11)	6592 (3)	34 (2)
C(4)	9274 (4)	5610 (11)	5518 (3)	42 (2)
C(5)	8228 (4)	4853 (10)	4669 (3)	34 (2)
C(6)	8220 (4)	5714 (10)	3627 (3)	39 (2)
C(8)	7105 (4)	5527 (10)	1845 (3)	31 (2)
C(9)	8157 (4)	5346 (10)	1241 (4)	29 (2)
C(10)	7561 (4)	5224 (11)	106 (3)	31 (2)
C(11)	6120 (4)	5305 (12)	38 (3)	35 (2)
C(12)	5986 (4)	4551 (10)	1118 (4)	29 (2)
C(13)	4758 (4)	4999 (11)	1374 (3)	36 (2)
C(14)	3780 (4)	5328 (11)	1600 (3)	34 (2)
C(15)	2541 (4)	5615 (12)	1901 (4)	37 (2)
C(16)	2544 (4)	4794 (9)	2965 (3)	32 (2)
C(17)	3512 (4)	5736 (10)	3843 (3)	36 (2)
C(18)	3460 (4)	5007 (11)	4931 (3)	33 (2)
C(19)	4479 (5)	5873 (9)	5798 (4)	38 (2)
C(20)	4420 (4)	5177 (13)	6883 (4)	47 (2)
O(1)	11662 (3)	5248 (8)	9102 (2)	50 (1)
O(2)	9635 (3)	4337 (8)	8800 (3)	54 (2)
O(3)	7367 (3)	4647 (6)	2834 (2)	34 (1)
O(4)	9285 (3)	5270 (8)	1659 (2)	44 (1)
O(5)	1585 (3)	4702 (7)	1095 (2)	39 (1)

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

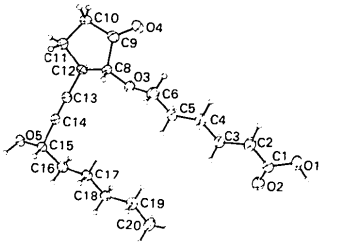

Fig. 1. Perspective drawing of CE1S displaying ellipsoids of 50% probability. The H atoms are drawn artificially small.

* Lists of structure factors, H-atom coordinates, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38232 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

source of the ambiguous peak positions in the *E* maps and the failure of the normal multisolution tangent refinement process. The planarity of the molecule is also responsible for the short *b* cell dimension, roughly twice the non-bonded C—C separation between molecules.

The molecular packing is illustrated in Fig. 2 and is held intact by a linear hydrogen bond between atoms O(1) and O(5) [O(1)···O(5) = 2·671 (6) and H(1)···O(5) = 1·73 (5) Å]. Combined with the twofold screw axis the effect of this hydrogen bonding is to produce planar networks of molecules separated by one half the *b*-axis length, 3·42 Å. Similar hydrogen bonding is found in other published prostaglandin (PG) structures and suggests that the mechanism of recognition/interaction of a prostaglandin and a biological receptor involves hydrogen bonding between the amino acids of the receptor and the O atoms of the prostaglandin.

The data in Table 3 compare the molecular structures of CE1S and various prostaglandins. The molecule adopts the 'hairpin' conformation characteristic of all published prostaglandin structures with the exception of the 'L-shaped' prostaglandin PGB_1 (DeTitta, Langs & Edmonds, 1979). An important conformational distinction between prostaglandin structures is made at the ring/chain junctions. A broad range of ring/α-chain geometries is revealed in Table 3. Although the chemical connectivity of CE1S is most similar to that of PGE_1, their ring/α-chain junction geometries are very different. The geometry of the ring/α-chain junction of CE1S is most similar to those of $PGF_{2\alpha}$ (Langs, Erman & DeTitta, 1977), PGF_{2I} (Chidester & Duchamp, 1974) and $PGF_{2\beta}$ (DeTitta *et al.*, 1980). This junction geometry thus appears to be very sensitive to the non-bonded interactions between O(9) of the cyclopentyl ring and the α chain (particularly atom 6).

The ring/ω-chain junction geometries are very similar for all molecules in Table 3 except for CE1S and PGB_1 (DeTitta *et al.*, 1979). The alkyne functional group of CE1S disallows a quantitative evaluation of the ring/ω-chain torsion angles. PGB_1 adopts an 'L-shape' conformation requiring the chain to be directed away from the ring so the hydroxyl on C(15) can be *cis* to the C(13)—C(14) double bond.

Additional degrees of conformational freedom result from the five-atom carbocycle. The conformation of this ring is defined by the endocyclic torsion angles given in Table 3. These data reveal that the five-atom

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)–C(2)	1·494 (7)	C(1)–O(1)	1·329 (5)
C(1)–O(2)	1·196 (6)	C(2)–C(3)	1·518 (6)
C(3)–C(4)	1·493 (7)	C(4)–C(5)	1·491 (6)
C(5)–C(6)	1·492 (7)	C(6)–O(3)	1·428 (6)
C(8)–C(9)	1·531 (7)	C(8)–C(12)	1·516 (7)
C(8)–O(3)	1·405 (6)	C(9)–C(10)	1·491 (6)
C(9)–O(4)	1·217 (5)	C(10)–C(11)	1·538 (6)
C(11)–C(12)	1·551 (7)	C(12)–C(13)	1·470 (7)
C(13)–C(14)	1·181 (7)	C(14)–C(15)	1·491 (7)
C(15)–C(16)	1·510 (7)	C(15)–O(5)	1·444 (6)
C(16)–C(17)	1·516 (6)	C(17)–C(18)	1·531 (7)
C(18)–C(19)	1·516 (6)	C(19)–C(20)	1·523 (7)
C(2)–C(1)–O(1)	111·9 (4)	C(2)–C(1)–O(2)	125·0 (4)
O(1)–C(1)–O(2)	123·1 (4)	C(1)–C(2)–C(3)	115·5 (5)
C(2)–C(3)–C(4)	113·3 (5)	C(3)–C(4)–C(5)	116·7 (5)
C(4)–C(5)–C(6)	113·5 (5)	C(5)–C(6)–O(3)	109·9 (5)
C(9)–C(8)–C(12)	102·4 (4)	C(9)–C(8)–O(3)	115·5 (4)
C(12)–C(8)–O(3)	111·2 (5)	C(8)–C(9)–C(10)	108·9 (3)
C(8)–C(9)–O(4)	123·4 (4)	C(10)–C(9)–O(4)	127·7 (5)
C(9)–C(10)–C(11)	104·9 (4)	C(10)–C(11)–C(12)	103·7 (3)
C(8)–C(12)–C(11)	102·0 (4)	C(8)–C(12)–C(13)	113·2 (5)
C(11)–C(12)–C(13)	114·6 (4)	C(12)–C(13)–C(14)	178·4 (6)
C(13)–C(14)–C(15)	176·5 (8)	C(14)–C(15)–C(16)	112·6 (4)
C(14)–C(15)–O(5)	106·3 (4)	C(16)–C(15)–O(5)	111·9 (5)
C(15)–C(16)–C(17)	114·0 (5)	C(16)–C(17)–C(18)	114·3 (5)
C(17)–C(18)–C(19)	113·8 (5)	C(18)–C(19)–C(20)	114·1 (5)
C(6)–O(3)–C(8)	114·9 (4)		

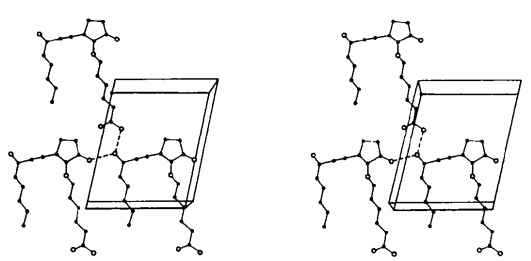

Fig. 2. Stereoview of the molecular packing illustrating the hydrogen bonding of the OH on C(15). The view direction is approximately parallel to the *b* axis.

Table 3. *Comparison of CE1S and published prostaglandin structures*

The α chain consists of atoms 1 (carboxyl C) through 7. The ω chain contains atoms 13 through 20. E.s.d.'s are 1·0° for CE1S.

Compound	Ring/chain junction geometry (°)[k] α chain		ω chain		Endocyclic torsion angles (°)[l]				
	T1	*TX1*	*T2*	*TX2*	*TR1*	*TR2*	*TR3*	*TR4*	*TR5*
CE1S[a]	−167	76	−77	165	1	−25	41	−40	25
PGE_1[b]	−69	168	−137	106	5	−28	40	−37	20
	−62	179	−142	98	5	−25	37	−34	19
PGE_2[c]	62	−61	−126	113	9	−28	35	−29	14
PGA_1[d]	−74	165	−135	107	−10	−2	13	−17	17
PGA_1[e]	−65	175	−132	113	−7	3	2	−6	8
PGB_1[f]	88	−89	−172	8	2	−2	2	−1	−1
$PGF_{2\alpha}$[g]	179	57	—	—	—	—	—	—	—
$PGF_{1\beta}$[h]	98	−145	133	−116	12	19	−41	47	−37
$PGF_{2\beta}$[i]	172	54	−129	115	1	−25	38	−37	22
PGF_{2I}[j]	−176	72	−118	124	−42	28	−3	−20	38
	169	56	−116	127	−51	33	−1	−31	48

(*a*) This work; (*b*) two independent molecules (Spek, 1977); (*c*) DeTitta *et al.* (1980); (*d*) monoclinic form (DeTitta *et al.*, 1979); (*e*) orthorhombic form (Edmonds & Duax, 1975); (*f*) DeTitta *et al.* (1979); (*g*) tris(hydroxymethyl)methylammonium salt (Langs *et al.*, 1977); (*h*) tri-*p*-bromobenzoate methyl ester (Abrahamsson, 1963); (*i*) DeTitta *et al.* (1980); (*j*) *p*-iodophenacyl ester of the 15-methyl compound (Chidester & Duchamp, 1974); (*k*) torsion-angle definitions: $T1 = \Omega(6\text{-}7\text{-}8\text{-}12)$; $TX1 = \Omega(6\text{-}7\text{-}8\text{-}9)$; $T2 = \Omega(8\text{-}12\text{-}13\text{-}14)$; $TX2 = \Omega(11\text{-}12\text{-}13\text{-}14)$; (*l*) torsion-angle definitions: $TR1 = \Omega(8\text{-}9\text{-}10\text{-}11)$; $TR2 = \Omega(9\text{-}10\text{-}11\text{-}12)$; $TR3 = \Omega(10\text{-}11\text{-}12\text{-}8)$; $TR4 = \Omega(11\text{-}12\text{-}8\text{-}9)$; $TR5 = \Omega(12\text{-}8\text{-}9\text{-}10)$.

rings of CE1S, PGE_1 (Spek, 1977), PGE_2 (DeTitta *et al.*, 1980), and $PGF_{2\beta}$ (DeTitta *et al.*, 1980) adopt C(12) envelope conformations. The cyclopentyl ring of PGF_{2I} (Chidester & Duchamp, 1974) adopts a C(9) envelope conformation. The two independent conformers of $PGF_{2\alpha}$ (Langs *et al.*, 1977) adopt envelope conformations, one a C(8) envelope and the other a C(9) envelope. The cyclopentyl ring of $PGF_{1\beta}$ (Abrahamsson, 1963) adopts a half-chair conformation. The cyclopentenyl rings of PGB_1 (DeTitta *et al.*, 1979) and of PGA_1 in both the monoclinic (DeTitta *et al.*, 1979) and orthorhombic (Edmonds & Duax, 1975) forms adopt relatively flat conformations.

In summary, the structural features of CE1S show both similarities and differences to those of previously reported prostaglandin structures. The relevance of solid-state, three-dimensional structural features to the solution properties of conformationally labile molecules, such as the prostaglandins, has been excessively discounted in the past. However, studies by Anderson and coworkers (Leovey & Anderson, 1975) suggest that the general structural features of $PGF_{2\alpha}$ in the crystalline state are maintained in solution. Circular dichroism spectra of aqueous $PGF_{2\alpha}$ are consistent with the 'hairpin' conformation for the chromophore defined by the C(5) through C(16) portion of the molecule. Lanthanide-induced shift NMR data are inconsistent with either an 'L-shape' or an extended conformation for the molecule. Also, the conformational specificities of the $PGF_{2\alpha}$ and PGE_2 receptors have been recently discussed in terms of the 'hairpin' alignment of the molecules (Anderson *et al.*, 1981). These data suggest that the structural features revealed by single-crystal diffraction are maintained by prostaglandin molecules in solution and are thus relevant to the solution properties. Until evidence to the contrary arises, we must likewise assume the conformation of CE1S determined by this study is descriptive of its favored conformation in solution.

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Acta Cryst. (1983). C**39**, 383–385

Structure of *endo*-3-Phenyl-3λ^5-phosphabicyclo[3.2.1]oct-6-ene 3-Oxide, $C_{13}H_{15}OP$

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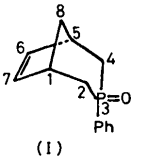
Abstract. $M_r = 218{\cdot}2$, orthorhombic, space group *Pbca*, $a = 9{\cdot}122$ (4), $b = 12{\cdot}960$ (3), $c = 19{\cdot}446$ (2) Å, $U = 2298{\cdot}9$ Å^3, $Z = 8$, $D_x = 1{\cdot}261$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}202$ mm^{-1}, $F(000) = 928$. Final $R = 0{\cdot}035$ for 880 observed reflections. The phosphorinane ring adopts a chair conformation which is flattened at the phosphorus end. The ring conformation, bond lengths and valence and torsion angles are compared with those in the *exo*-3-phenyl isomer.

Introduction. In a previous study, the synthesis of both the title compound (I) and its *exo*-3-phenyl isomer (II) were described (Haque, Horne, Cremer & Most, 1981). The isomer assignments were made on the basis of NMR studies and confirmed by a crystal-structure analysis of the *exo*-3-phenyl compound. The purpose of



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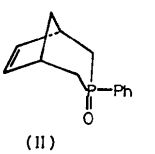

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