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

O(1)–C(2)	1·328 (5)	O(1)–C(7a)	1·452 (5)
C(2)–C(3)	1·348 (6)	C(3)–C(4)	1·476 (6)
C(3)–C(8)	1·470 (6)	C(4)–C(4a)	1·514 (6)
C(4)–O(12)	1·468 (5)	C(4a)–C(5)	1·516 (6)
C(4a)–C(7a)	1·513 (6)	C(5)–C(6)	1·506 (7)
C(6)–O(7)	1·461 (6)	O(7)–C(7a)	1·365 (6)
C(8)–O(9)	1·327 (5)	C(8)–O(11)	1·195 (5)
O(9)–C(10)	1·436 (6)	O(12)–C(13)	1·326 (5)
C(13)–O(14)	1·201 (5)	C(13)–C(15)	1·489 (6)
C(15)–O(16)	1·472 (5)	C(15)–C(20)	1·525 (5)
C(15)–C(21)	1·547 (6)	O(16)–C(17)	1·362 (5)
C(17)–C(18)	1·499 (5)	C(17)–O(25)	1·202 (5)
C(18)–C(19)	1·552 (6)	C(18)–C(21)	1·558 (6)
C(18)–C(24)	1·502 (6)	C(19)–C(20)	1·539 (6)
C(21)–C(22)	1·542 (6)	C(21)–C(23)	1·527 (5)
C(2)–O(1)–C(7a)	120·3 (3)	O(1)–C(2)–C(3)	125·9 (4)
C(2)–C(3)–C(4)	119·9 (4)	C(2)–C(3)–C(8)	120·9 (4)
C(4)–C(3)–C(8)	119·2 (4)	C(3)–C(4)–C(4a)	110·7 (3)
C(3)–C(4)–O(12)	106·2 (3)	C(4a)–C(4)–O(12)	107·8 (3)
C(4)–C(4a)–C(5)	115·6 (4)	C(4)–C(4a)–C(7a)	114·2 (4)
C(5)–C(4a)–C(7a)	101·0 (4)	C(4a)–C(5)–C(6)	103·3 (4)
C(5)–C(6)–O(7)	106·4 (4)	C(6)–O(7)–C(7a)	109·0 (3)
O(1)–C(7a)–C(4a)	112·2 (3)	O(1)–C(7a)–O(7)	107·3 (4)
C(4a)–C(7a)–O(7)	106·9 (4)	C(3)–C(8)–O(9)	112·9 (4)
C(3)–C(8)–O(11)	123·9 (4)	O(9)–C(8)–O(11)	123·2 (4)
C(8)–O(9)–C(10)	119·3 (4)	C(4)–O(12)–C(13)	119·7 (3)
O(12)–C(13)–O(14)	125·0 (4)	O(12)–C(13)–C(15)	108·3 (3)
O(14)–C(13)–C(15)	126·6 (4)	C(13)–C(15)–O(16)	108·4 (3)
C(13)–C(15)–C(20)	117·3 (4)	O(16)–C(15)–C(20)	104·7 (3)
C(13)–C(15)–C(21)	119·0 (3)	O(16)–C(15)–C(21)	101·9 (3)
C(20)–C(15)–C(21)	103·6 (3)	C(15)–O(16)–C(17)	106·5 (3)
O(16)–C(17)–C(18)	107·4 (3)	O(16)–C(17)–O(25)	122·0 (3)
C(18)–C(17)–O(25)	130·6 (4)	C(17)–C(18)–C(19)	103·4 (3)
C(17)–C(18)–C(21)	99·1 (3)	C(19)–C(18)–C(21)	102·3 (3)
C(17)–C(18)–C(24)	115·3 (4)	C(19)–C(18)–C(24)	116·0 (3)
C(21)–C(18)–C(24)	118·3 (4)	C(18)–C(19)–C(20)	103·8 (3)
C(15)–C(20)–C(19)	102·1 (3)	C(15)–C(21)–C(18)	91·8 (3)
C(15)–C(21)–C(22)	112·3 (3)	C(18)–C(21)–C(22)	113·6 (3)
C(15)–C(21)–C(23)	116·1 (3)	C(18)–C(21)–C(23)	113·7 (3)

are given in Table 1,* and bond lengths and angles in Table 2. Fig. 1 shows the molecule and numbering scheme.

Related literature. For the preparation of the compound see Tietze & Glüsenkamp (1983). For the preparation and structure of a related compound see Tietze, Glüsenkamp, Harms, Remberg & Sheldrick (1982).

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Structure of a Photolysis Product

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Abstract. Methyl (+)-1β-hydroxy-7α-methoxy-5β-trityloxymethyl-4aβ,7,8,8aβ-tetrahydro-1H,5H-pyrano-[4,3-c]pyran-4-carboxylate, $C_{31}H_{32}O_7$, $M_r = 516·6$, orthorhombic, $P2_12_12_1$, $a = 8·424$ (1), $b = 14·773$ (2), $c = 22·165$ (2) Å, $U = 2758$ Å^3, $Z = 4$, $D_x = 1·244$ Mg m^{-3}, λ(Mo Kα) = 0·71069 Å, $\mu = 0·077$ mm^{-1}, $F(000) = 1096$, $T = 298$ K, $R = 0·079$ for 1447 reflections. The title compound is the main product of a photolysis reaction. Its absolute configuration is deduced from the known configuration at C(5) and C(7).

Experimental. Crystal size 0·1 × 0·1 × 0·3 mm. Stoe–Siemens four-circle diffractometer, monochromated

Table 1. Atomic coordinates (×10⁴) and isotropic thermal parameters (Å² × 10³)

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}*
C(1)	6224 (9)	5948 (6)	10906 (4)	50 (3)
O(2)	5757 (7)	5236 (5)	11345 (3)	70 (3)
C(3)	4202 (10)	5020 (7)	11366 (3)	49 (3)
C(4)	3052 (10)	5308 (6)	11007 (3)	40 (3)
C(4a)	3404 (9)	6050 (5)	10556 (3)	36 (3)
C(5)	3686 (10)	5723 (5)	9912 (3)	33 (3)
O(6)	3996 (7)	6469 (4)	9526 (2)	42 (2)
C(7)	5347 (10)	6969 (6)	9669 (4)	48 (3)
C(8)	5362 (11)	7305 (6)	10314 (4)	51 (3)
C(8a)	4883 (9)	6576 (5)	10764 (3)	40 (3)
O(9)	7495 (7)	6381 (4)	11177 (3)	67 (3)
C(10)	1380 (10)	5062 (7)	11095 (4)	51 (3)
O(11)	1246 (8)	4352 (5)	11478 (3)	75 (3)
C(12)	−401 (15)	4121 (10)	11640 (7)	139 (7)
O(13)	308 (7)	5431 (4)	10884 (3)	68 (3)
C(14)	2370 (9)	5188 (5)	9640 (3)	36 (3)
O(15)	3040 (6)	4776 (4)	9112 (2)	44 (2)
C(16)	2000 (10)	4366 (6)	8666 (4)	40 (3)
O(17)	6745 (7)	6462 (4)	9580 (2)	52 (2)
C(18)	6951 (14)	6185 (8)	8966 (4)	74 (4)
C(101)	4711 (9)	3721 (5)	8397 (3)	86 (5)
C(102)	5750	3313	7989	114 (6)
C(103)	5235	3100	7408	93 (6)
C(104)	3681	3296	7234	92 (5)
C(105)	2641	3704	7642	78 (5)
C(106)	3156	3917	8223	48 (3)
C(201)	1358 (8)	2747 (5)	8966 (3)	62 (4)
C(202)	419	2106	9260	92 (5)
C(203)	−949	2376	9565	108 (7)
C(204)	−1379	3288	9576	102 (6)
C(205)	−441	3929	9283	79 (5)
C(206)	928	3659	8977	58 (4)
C(301)	−346 (8)	4865 (5)	8043 (3)	62 (4)
C(302)	−1148	5513	7702	79 (5)
C(303)	−546	6390	7657	96 (6)
C(304)	859	6619	7953	81 (5)
C(305)	1661	5971	8295	56 (4)
C(306)	1059	5094	8340	47 (3)

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

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

H—O(9)	1·182 (80)	C(1)—O(2)	1·485 (11)
C(1)—C(8a)	1·495 (11)	C(1)—O(9)	1·384 (10)
O(2)—C(3)	1·349 (10)	C(3)—C(4)	1·323 (11)
C(4)—C(4a)	1·512 (11)	C(4)—C(10)	1·469 (12)
C(4a)—C(5)	1·527 (10)	C(4a)—C(8a)	1·540 (11)
C(5)—O(6)	1·418 (9)	C(5)—C(14)	1·489 (11)
O(6)—C(7)	1·393 (10)	C(7)—C(8)	1·511 (12)
C(7)—O(17)	1·410 (10)	C(8)—C(8a)	1·522 (12)
C(10)—O(11)	1·353 (11)	C(10)—O(13)	1·154 (11)
O(11)—C(12)	1·474 (14)	C(14)—O(15)	1·435 (9)
O(15)—C(16)	1·454 (9)	O(17)—C(18)	1·432 (11)
C(106)—C(16)	1·534 (11)	C(206)—C(16)	1·544 (11)
C(306)—C(16)	1·519 (11)		

O(2)—C(1)—C(8a)	112·2 (6)	O(2)—C(1)—O(9)	104·4 (6)
C(8a)—C(1)—O(9)	112·9 (7)	C(1)—O(2)—C(3)	116·6 (6)
O(2)—C(3)—C(4)	127·9 (8)	C(3)—C(4)—C(4a)	119·1 (7)
C(3)—C(4)—C(10)	122·8 (7)	C(4a)—C(4)—C(10)	117·1 (7)
C(4)—C(4a)—C(5)	114·8 (6)	C(4)—C(4a)—C(8a)	109·1 (6)
C(5)—C(4a)—C(8a)	108·3 (6)	C(4a)—C(5)—O(6)	110·3 (6)
C(4a)—C(5)—C(14)	115·5 (6)	O(6)—C(5)—C(14)	107·9 (6)
C(5)—O(6)—C(7)	115·2 (6)	O(6)—C(7)—C(8)	113·3 (7)
O(6)—C(7)—O(17)	111·6 (7)	C(8)—C(7)—O(17)	107·5 (7)
C(7)—C(8)—C(8a)	112·7 (7)	C(1)—C(8a)—C(4a)	111·2 (7)
C(1)—C(8a)—C(8)	112·2 (7)	C(4a)—C(8a)—C(8)	112·0 (6)
H—O(9)—C(1)	80·0 (39)	C(4)—C(10)—O(11)	110·8 (7)
C(4)—C(10)—O(13)	125·4 (8)	O(11)—C(10)—O(13)	123·8 (8)
C(10)—O(11)—C(12)	114·2 (8)	C(5)—C(14)—O(15)	105·2 (6)
C(14)—O(15)—C(16)	119·6 (6)	O(15)—C(16)—C(106)	103·5 (6)
O(15)—C(16)—C(206)	109·3 (6)	C(106)—C(16)—C(206)	111·4 (6)
O(15)—C(16)—C(306)	110·1 (6)	C(106)—C(16)—C(306)	109·5 (6)
C(206)—C(16)—C(306)	112·7 (6)	C(7)—O(17)—C(18)	112·7 (7)
C(16)—C(106)—C(101)	120·6 (4)	C(16)—C(106)—C(105)	119·4 (4)
C(16)—C(206)—C(201)	119·5 (4)	C(16)—C(206)—C(205)	120·4 (4)
C(16)—C(306)—C(301)	119·7 (4)	C(16)—C(306)—C(305)	120·1 (4)

Mo $K\alpha$ radiation, profile-fitting mode (Clegg, 1981). 2098 reflections, $2\theta_{max}$ 40°, $+h$ $+k$ $+l$, three check reflections with no intensity change. 2035 unique reflections ($R_{int} = 0.018$) of which 1447 with $F > 3\sigma(F)$ used for all calculations; program system *SHELXTL* (Sheldrick, 1978). Index ranges $h \leq 8$, $k \leq 15$, $l \leq 23$. Cell constants refined from $\pm 2\theta$ values of 24 reflections in the range 20–25°. Absorption and extinction corrections not necessary.

Structure solution by multisolution direct methods. Refinement on F to $R = 0.079$, $wR = 0.085$; all non-H atoms anisotropic, phenyl groups as rigid hexagons (C—C 1·395 Å), H atoms included using a riding model [C—H 0·96 Å, $U(\text{H}) = 1·2$ $U_{eq}(\text{C})$], 317 parameters, $S = 1·56$, weighting scheme $w^{-1} = \sigma^2(F) + 0·00120F^2$ which gave a featureless analysis of variance, max. $\Delta/\sigma = 0·014$, max. and min. heights in the final $\Delta\rho$ map 0·31 and $-0·31$ e Å^{-3} respectively. The main cause of the relatively high R indices was probably the very small crystal (for Mo $K\alpha$ radiation). This is indicated by the unusually high value of $R_{sigma} = \Sigma\sigma(F)/\Sigma F = 0·063$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The atomic parameters are given in Table 1,* and bond lengths and angles in Table 2. Fig. 1 shows the molecule and numbering scheme.

Related literature. For the preparation of the compound see Tietze, Glüsenkamp, Nakane & Hutchinson (1982);
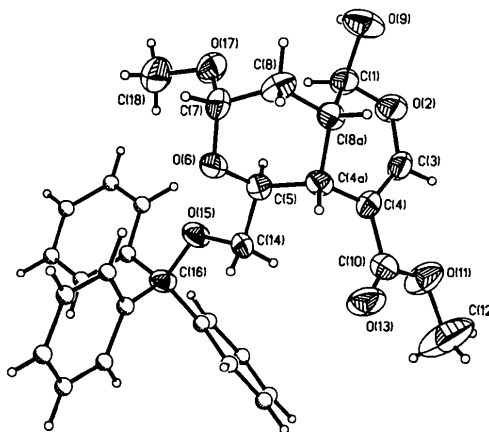
Fig. 1. The asymmetric unit of the title compound, showing the numbering scheme.

it represents a stage in the synthesis of (+)-sarracenin. For the structure of the latter see Miles *et al.* (1976).

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Structure of Tetraphenylphosphonium Chloride

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Abstract. $C_{24}H_{20}P^+.Cl^-$, $M_r = 374 \cdot 85$, monoclinic, $P2_1/n$, $a = 9 \cdot 3069$ (7), $b = 9 \cdot 6235$ (5), $c = 22 \cdot 225$ (2) Å, $\beta = 99 \cdot 248$ (4)°, $V = 1964 \cdot 7$ (2) Å³, $Z = 4$, $D_x = 1 \cdot 27$ Mg m⁻³, $\lambda(Cu K\alpha) = 1 \cdot 5418$ Å, $\mu = 2 \cdot 50$ mm⁻¹, $F(000) = 784$, $T = 294$ K, $R = 0 \cdot 038$ for 2865 unique reflections. The salt, isolated as an impurity in the preparation of $(Ph_4P)^+[S—(p\text{-}tolyl)]^-$, is not found to be isostructural with the previously reported structure of $(Ph_4P)^+Br^-$ or powder studies of $(Ph_4P)^+I^-$ and $(Ph_4As)^+I^-$. The average P—C bond length is $1 \cdot 788$ (2) Å and dimensions of the phenyl rings are considered normal.

Experimental. Colourless block (cut), $0 \cdot 3 \times 0 \cdot 5 \times 0 \cdot 5$ mm, Enraf–Nonius CAD-4F diffractometer, Ni pre-filtered Cu $K\alpha$ radiation; lattice parameters from least-squares refinement of 25 accurately centered reflections with $40 \le \theta \le 56°$; space group uniquely determined from absences ($h0l$ $h + l = 2n + 1$, $0k0$ $k = 2n + 1$); 3337 unique reflections collected, 2865 considered observed at the $3\sigma(I)$ level [$\sigma(I)$ from counting statistics], $\theta_{max} = 65°$, $\omega/2\theta$ scans, scan range of $1 \cdot 5(0 \cdot 66 + 0 \cdot 142\tan\theta)°$, variable scan speed $0 \cdot 7°$–$3 \cdot 4°$ min⁻¹; three standard reflections ($16\bar{3}$, $1,\bar{2},\overline{12}$, $3,\bar{1},10$) measured every 1500 s of X-ray exposure time, max. variation $+5 \cdot 0\%$, data collected: $+h$, $-k$, $\pm l$ to max. indices of 10, 11, 26. Data corrected for background, Lp, drift in standards and absorption (Walker & Stuart, 1983); min., max. absorption corrections of $0 \cdot 79$ and $1 \cdot 24$. Structure solved by direct methods, *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and difference Fourier syntheses, refined by full-matrix least squares based on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$, w defined as $[\sigma^2(F_o) + 0 \cdot 00001(F^2)]^{-1}$, *XRAY76* system of programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); H atoms included in calculated positions with isotropic thermal parameters set to $1 \cdot 1$ times B_{eq} of the bonded atom, H parameters not refined, all non-H atoms refined with anisotropic thermal parameters. Model converged with: 2865 observations, 236 variables, $R = 0 \cdot 038$, $wR = 0 \cdot 038$, max. $\Delta/\sigma = 0 \cdot 67$ for E but all others $<0 \cdot 009$, $S = 1 \cdot 51$, isotropic extinction parameter $(E) = 9 \cdot 9$ (5) $\times 10^{-4}$, max. residual electron density $= 0 \cdot 28$ e Å⁻³ associated with P. Scattering factors were those of Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H atoms. Anomalous-dispersion corrections included for non-H atoms (*International Tables for X-ray Crystallography*, 1974). The closest interionic contact distance is $2 \cdot 603$ Å between H(33) and H(36) (at $1\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$). An *ORTEP* plot of the unit cell is shown in Fig. 1, atomic coordinates are given in Table 1, and bond lengths and angles are listed in Table 2†

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† Lists of structure factors, anisotropic thermal parameters for the non-H atoms, and positional and isotropic thermal parameters for the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42968 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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