Data collection

Siemens *R3m/V* diffractometer
2θ–θ scans
Absorption correction: none
2064 measured reflections
1027 independent reflections
879 observed reflections [$F > 3\sigma(F)$]

$R_{\text{int}} = 0.0172$
$\theta_{\text{max}} = 25.5°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 14$
2 standard reflections monitored every 98 reflections

Refinement

Refinement on F
Final $R = 0.039$
$wR = 0.055$
$S = 0.99$
156 parameters
Riding model, C—H 0.96 Å, free isotropic U; methyl H atoms located from ΔF map, refined isotropically

$w = [\sigma^2(F) + 0.0024F^2]^{-1}$
$(\Delta/\sigma)_{\text{max}} = 0.030$
$\Delta\rho_{\text{max}} = 0.11$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.19$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Program used to solve and refine structure: *SHELXTL PLUS* (Sheldrick, 1990).

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

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1)	0.1550 (4)	0.3321 (3)	1.2706 (2)	0.079 (1)
O(1)	0.1926 (5)	0.2342 (3)	1.3158 (2)	0.120 (1)
O(2)	0.1345 (5)	0.4289 (3)	1.3207 (2)	0.113 (1)
O(3)	0.1242 (3)	0.1017 (2)	0.6575 (1)	0.078 (1)
C(1)	0.1490 (4)	0.2024 (2)	0.9839 (2)	0.053 (1)
C(2)	0.1054 (4)	0.0821 (3)	0.9500 (2)	0.062 (1)
C(3)	0.0960 (3)	0.0509 (3)	0.8412 (2)	0.064 (1)
C(4)	0.1345 (3)	0.1411 (3)	0.7635 (2)	0.059 (1)
C(5)	0.1793 (3)	0.2603 (2)	0.7943 (2)	0.061 (1)
C(6)	0.1863 (3)	0.2902 (2)	0.9041 (2)	0.058 (1)
C(7)	0.1581 (3)	0.2271 (3)	1.1009 (2)	0.059 (1)
C(8)	0.1383 (3)	0.3352 (3)	1.1515 (2)	0.060 (1)
C(9)	0.0907 (5)	0.4600 (3)	1.1072 (3)	0.077 (1)
C(10)	0.1574 (6)	0.1915 (3)	0.5759 (2)	0.085 (1)
H(9*A*)	0.0252 (49)	0.4492 (36)	1.0402 (32)	0.105 (12)
H(9*B*)	0.1874 (70)	0.5031 (44)	1.1056 (46)	0.147 (20)
H(9*C*)	0.0136 (47)	0.5090 (30)	1.1650 (27)	0.099 (10)
H(10*A*)	0.1416 (52)	0.1415 (33)	0.5080 (29)	0.107 (12)
H(10*B*)	0.2884 (59)	0.2267 (38)	0.5831 (36)	0.119 (14)
H(10*C*)	0.0665 (50)	0.2533 (31)	0.5780 (31)	0.091 (11)

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

N(1)—O(1)	1.221 (4)	N(1)—O(2)	1.217 (4)
N(1)—C(8)	1.474 (3)	O(3)—C(4)	1.375 (3)
O(3)—C(10)	1.414 (4)	C(1)—C(2)	1.393 (4)
C(1)—C(6)	1.389 (3)	C(1)—C(7)	1.467 (3)
C(2)—C(3)	1.384 (4)	C(3)—C(4)	1.390 (4)
C(4)—C(5)	1.373 (4)	C(5)—C(6)	1.392 (3)
C(7)—C(8)	1.324 (4)	C(8)—C(9)	1.486 (4)
C(9)—H(9*A*)	0.96 (4)	C(10)—H(10*A*)	1.00 (4)
C(9)—H(9*B*)	0.85 (5)	C(10)—H(10*B*)	1.04 (4)
C(9)—H(9*C*)	1.05 (3)	C(10)—H(10*C*)	0.94 (4)
O(1)—N(1)—O(2)	122.0 (3)	O(1)—N(1)—C(8)	119.6 (3)
O(2)—N(1)—C(8)	118.4 (3)	C(4)—O(3)—C(10)	117.2 (2)
C(2)—C(1)—C(6)	117.4 (2)	C(2)—C(1)—C(7)	118.2 (2)
C(6)—C(1)—C(7)	124.4 (2)	C(1)—C(2)—C(3)	121.7 (2)
C(2)—C(3)—C(4)	119.3 (3)	O(3)—C(4)—C(3)	115.4 (2)
O(3)—C(4)—C(5)	124.1 (2)	C(3)—C(4)—C(5)	120.4 (2)
C(4)—C(5)—C(6)	119.5 (2)	C(1)—C(6)—C(5)	121.7 (2)
C(1)—C(7)—C(8)	128.0 (2)	N(1)—C(8)—C(7)	116.1 (2)
N(1)—C(8)—C(9)	113.9 (2)	C(7)—C(8)—C(9)	129.8 (2)
H(9*A*)—C(9)—H(9*B*)	118 (4)	H(10*A*)—C(10)—H(10*B*)	112 (3)
H(9*A*)—C(9)—H(9*C*)	112 (3)	H(10*A*)—C(10)—H(10*C*)	108 (3)
H(9*B*)—C(9)—H(9*C*)	102 (4)	H(10*B*)—C(10)—H(10*C*)	114 (3)

One of the authors (DB) thanks Fundación Andes for funding the purchase of a single-crystal diffractometer.

Lists of structure factors, anisotropic thermal parameters and complete H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55486 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1007]

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Acta Cryst. (1993). C**49**, 388–391

Structure of Ethyltriphenylphosphonium Triiodide, $[P(C_2H_5)(C_6H_5)_3]I_3$

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Abstract

The title compound was obtained unexpectedly from a mixture of $KReO_4$, triphenylphosphine and excess HI in ethanol. The crystal contains the tetrahedral $[P(C_2H_5)(C_6H_5)_3]^+$ cation in which the P—C distances range from 1.789 (13) to 1.819 (14) Å and the C—P—C angles from 108.3 (6) to 110.5 (6)°. The I_3^-

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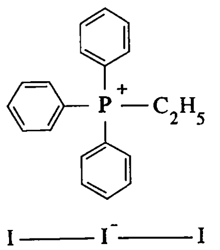
counterion is roughly linear [I—I—I = 176.89 (5)°] and the I—I distances are 2.908 (1) and 2.948 (1) Å. Slightly puckered chains of I_3^- ions with interionic I···I contacts of 4.007 (1) Å form infinite layers separated by layers of phosphonium cations in the unit cell.

Comment

In an attempt to develop new synthetic routes to the oxo-rhenium complex $ReOI_3[P(C_6H_5)_3]_2$, $KReO_4$ (0.54 g, 1.81 mmol) was reacted with triphenylphosphine (5.21 g, 19.9 mmol) and concentrated HI (10 ml, 5.5 mmol) in ethanol (75 ml). The suspension of the green intermediate $ReO(OC_2H_5)I_2[P(C_6H_5)_3]_2$ (Ciani, D'Alfonso, Romiti, Sironi & Freni, 1983) was refluxed for 22 h without significant color change. Upon the addition of a second 10 ml portion of concentrated HI, the reaction mixture turned brownish. Two hours later, a brown suspension was obtained and the mixture was filtered. The solid was identified as unreacted $ReO(OC_2H_5)I_2[P(C_6H_5)_3]_2$. Thin orange plates crystallized out from the orange filtrate. These were identified by X-ray diffraction as the triiodide salt of the ethyltriphenylphosphonium ion (1). The phosphonium moiety was produced from the tertiary phosphine by a reaction known to occur with alcohols under acidic conditions (Smith, 1979). I^- was oxidized to I_3^- by either ReO_4^- or molecular oxygen.



(1)

The P atom in the cation (Fig. 1) shows the expected tetrahedral coordination (Table 2). The P—C(ethyl) [1.819 (14) Å] and P—C(phenyl) [1.789 (13)–1.805 (13), mean 1.796 Å] distances compare well with those reported previously (Ferguson, McCrindle, McAlees & Rice, 1988; Fleming, Shaikh, Skelton & White, 1979). Details of the geometry of the phenyl rings are provided in the supplementary material. The phenyl rings are planar to within the experimental error [mean C-to-plane distance = 0.006, maximum 0.021 (15) Å], but the P atom is much more distant from these planes [0.081 (3), 0.120 (4) and 0.064 (4) Å]. The $P—CH_2—CH_3$ angle [114.0 (10)°] is slightly greater than tetrahedral, in agreement with earlier results (Ferguson *et al.*, 1988; Fleming *et al.*, 1979).

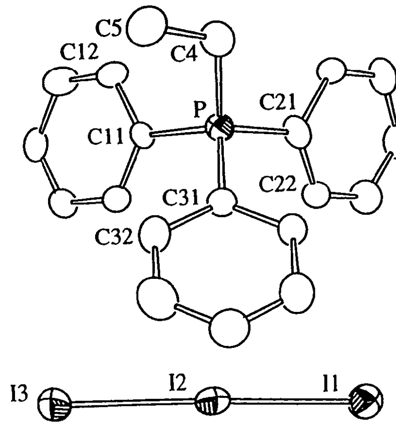


Fig. 1. Structure and numbering scheme of the $[P(C_2H_5)(C_6H_5)_3]^+$ cation and I_3^- anion. The atoms in the phenyl rings are assigned C(*ij*) symbols where *i* is the ring number and *j* corresponds to sequential numbering around the ring, starting with *j* = 1 for the C atoms bonded to P. Ellipsoids correspond to 50% probability. H atoms are omitted for simplicity.

The I_3^- ion (Fig. 1) is roughly linear [I—I—I = 176.89 (5)°] and the I—I bond lengths [2.908 (1), 2.948 (1) Å] are similar to those found in the $[As(C_6H_5)_4]^+$ and $[\{(C_6H_5)_3AsO\}_2H]^+$ salts (Runsink, Swen-Walstra & Migchelsen, 1972; Beagley, El-Sayrafi, Gott, Kelly, McAuliffe, Mackie, MacRory & Pritchard, 1988). The difference between the I—I distances although statistically very significant, is still relatively small as differences of > 0.2 Å are observed in compounds where hydrogen bonding and/or strong interionic I···I interactions are found (Tebbe, Freckmann, Hörner, Hiller & Strähle, 1985). The I_3^- ions in the present salt are not totally independent; they are connected into infinite chains *via* an I(1)···I(3) contact of 4.007 (1) Å, shorter than the sum of the van der Waals radii (4.30 Å; Cotton &

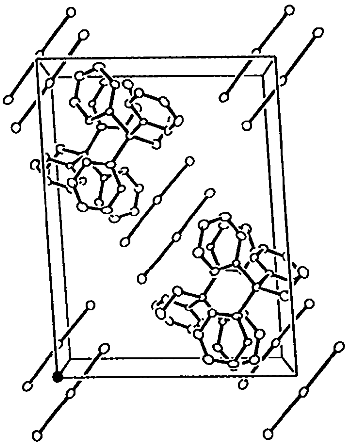


Fig. 2. View of the unit cell down the *b* axis. The origin is shown as a black dot. The *a* (horizontal) and *c* (vertical) axes are in the plane of the figure, whereas *b* points away from the reader.

Wilkinson, 1988). These slightly puckered chains [angles of 168.51 (4) and 151.86 (4)° at I(3) and I(1), respectively] define infinite layers parallel to the *ac* diagonal of the unit cell (Fig. 2). These layers are separated by layers of $[P(C_2H_5)(C_6H_5)_3]^+$ cations in which the cations interact by normal van der Waals contacts.

Experimental

Crystal data

$C_{20}H_{20}P^+.I_3^-$
$M_r = 672.07$
Monoclinic
$P2_1/n$
$a = 11.749$ (3) Å
$b = 12.028$ (2) Å
$c = 15.652$ (6) Å
$\beta = 93.26$ (3)°
$V = 2208.2$ (11) Å^3
$Z = 4$
$D_x = 2.021$ Mg m^{-3}
$D_m = 1.98$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 10.0–12.5°$
$\mu = 34.4$ mm^{-1}
$T = 298$ K
Thin plates
0.39 × 0.21 × 0.01 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
Gaussian by integration from crystal shape (10 × 10 × 10)
$T_{\min} = 0.08$, $T_{\max} = 0.71$
4330 measured reflections
4179 independent reflections

2181 observed reflections [$I \geq 3\sigma(I)$]
$R_{\text{int}} = 0.031$
$\theta_{\max} = 70°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -19 \rightarrow 19$
7 standard reflections
frequency: 60 min
intensity variation: 3%

Refinement

Refinement on F
Final $R = 0.049$
$wR = 0.048$
$S = 1.73$
2181 reflections
343 parameters
Hydrogen positions calculated
$w = 1/[\sigma^2(F)+0.0001F^2]$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}
Atomic scattering factors from Cromer & Liberman (1970) (non-H atoms) and Stewart, Davidson & Simpson (1965) (H atoms)

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

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
I(1)	0.37537 (8)	0.21798 (10)	0.30044 (6)	0.067
I(2)	0.53710 (7)	0.28920 (9)	0.43707 (6)	0.050
I(3)	0.69645 (9)	0.35166 (11)	0.58142 (7)	0.079
P	0.8633 (3)	0.1349 (3)	0.2742 (2)	0.040
C(4)	0.9740 (12)	0.0365 (12)	0.2489 (9)	0.056
C(5)	1.0569 (13)	0.0102 (13)	0.3234 (10)	0.071
C(11)	0.9265 (10)	0.2624 (10)	0.3131 (7)	0.033
C(12)	1.0319 (10)	0.2960 (12)	0.2842 (8)	0.046
C(13)	1.0772 (12)	0.3976 (13)	0.3092 (9)	0.057
C(14)	1.0221 (12)	0.4620 (12)	0.3667 (9)	0.053
C(15)	0.9181 (11)	0.4299 (12)	0.3959 (8)	0.045
C(16)	0.8713 (10)	0.3283 (12)	0.3689 (8)	0.042
C(21)	0.7724 (12)	0.1651 (11)	0.1802 (7)	0.046
C(22)	0.6687 (11)	0.2173 (13)	0.1883 (8)	0.049
C(23)	0.6035 (12)	0.2474 (13)	0.1197 (10)	0.060
C(24)	0.6381 (13)	0.2266 (13)	0.0393 (10)	0.059
C(25)	0.7420 (14)	0.1753 (14)	0.0279 (8)	0.063
C(26)	0.8100 (10)	0.1442 (12)	0.0989 (8)	0.047
C(31)	0.7802 (10)	0.0745 (11)	0.3545 (7)	0.040
C(32)	0.8106 (12)	0.0855 (13)	0.4417 (8)	0.057
C(33)	0.7448 (14)	0.0348 (13)	0.5019 (9)	0.064
C(34)	0.6531 (12)	−0.0295 (13)	0.4769 (9)	0.057
C(35)	0.6234 (12)	−0.0416 (12)	0.3918 (9)	0.056
C(36)	0.6861 (11)	0.0097 (12)	0.3292 (8)	0.048

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

I(1)—I(2)	2.908 (1)	I(2)—I(3)	2.948 (1)
P—C(11)	1.795 (12)	P—C(21)	1.805 (13)
P—C(31)	1.789 (13)	P—C(4)	1.819 (14)
C(4)—C(5)	1.510 (21)	I(3)—I(1)$^{\text{i}}$	4.007 (1)
I(1)—I(2)—I(3)	176.89 (5)	C(11)—P—C(21)	108.6 (6)
C(4)—P—C(11)	110.0 (6)	C(11)—P—C(31)	109.9 (6)
C(4)—P—C(21)	110.5 (6)	C(21)—P—C(31)	109.5 (6)
C(4)—P—C(31)	108.3 (6)	P—C(4)—C(5)	114.0 (10)
P—C(11)—C(12)	119.5 (9)	P—C(11)—C(16)	120.6 (9)
P—C(21)—C(22)	120.0 (10)	P—C(21)—C(26)	120.3 (10)
P—C(31)—C(32)	121.9 (10)	P—C(31)—C(36)	118.9 (10)
I(2)—I(3)—I(1)$^{\text{i}}$	151.86 (4)	I(2)—I(1)—I(3)$^{\text{ii}}$	168.51 (4)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

D_m was measured by flotation in CCl_4/1,1,2,2-tetrabromoethane. The data were corrected for Lp. The space group $P2_1/n$ was uniquely defined from the monoclinic Laue symmetry and systematic absences ($h0l$ $h+l \neq 2n$, $0k0$ $k \neq 2n$). The structure was solved by the heavy-atom method. The first I atom was located from a Patterson map; all other non-H atoms were found by successive ΔF maps. The non-H atoms were refined anisotropically by full-matrix least-squares methods. The H atoms were fixed at idealized positions (0.95 Å, U = 0.076, 0.089 and 0.101 Å^2 for phenyl, CH_2 and CH_3, respectively). Their parameters were not refined, but their coordinates were recalculated after each cycle. The programs used are listed elsewhere (Authier-Martin & Beauchamp. 1977). Anomalous-dispersion terms were taken from Cromer (1965).

We wish to thank A.-M. Lebuis and M. Simard for their assistance in collecting the X-ray data. The financial support of the Natural Sciences and Engineering Research Council of Canada is also acknowledged.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55510 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1009]

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Acta Cryst. (1993). C**49**, 391–392

Structure of 1-Deoxycastanospermine

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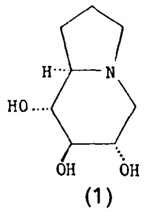
Abstract

The crystal structure of (6*S*,7*R*,8*R*,8a*R*)-6,7,8-trihydroxyoctahydroindolizine, $C_8H_{15}NO_3$, has been determined by X-ray diffraction. The six-membered ring is in the chair form and the puckering parameters [Cremer & Pople (1975). *J. Am. Chem. Soc.* **97**, 1354–1358] are $Q = 0.574$ Å, $\theta = 8.3°$, $\varphi_2 = 13.9°$. The five-membered ring is in the envelope form with $Q = 0.428$ Å and $\varphi_2 = 9.2°$.

Comment

The naturally occurring polyhydroxylated indolizidine alkaloid castanospermine is a potent inhibitor of glycosidase enzymes, particularly those involved in the Golgi processing of the N-linked oligosaccharide moiety of glycoproteins in mammals. (Pan *et al.*, 1983; Szumilo, Kaushal & Elbein, 1986; Campbell, Molyneux & Jones, 1987). It has since attracted considerable interest because of its antiviral activity against HIV and related viruses (Tyms *et al.*, 1987; Sunkara, Bowlin, Liu & Sjoerdsma, 1987; Gunters *et al.*, 1987; Walker *et al.*, 1987). The enantiospecific synthesis of polyhydroxylated indolizidines related to castanospermine has also received much attention (Reymond, Pinkerton & Vogel, 1991). The synthesis of the title compound (1) has been reported by Hendry, Hough & Richardson (1988). We now report the X-ray crystal structure of the compound. The crystal is orthorhombic, space group $P2_12_12_1$. The structure was solved by direct methods using *SHELXTL-Plus* (Siemens Analytical X-ray Instruments, Inc., 1990). Coordinates of non-H atoms are given in Table 1. Selected bond lengths and angles are given in Table 2. The molecule and its atomic numbering is shown in Fig. 1. Crystal packing and hydrogen bonding are shown in Fig. 2. These figures also depict the correct absolute configuration of the molecule as established by the synthesis of the compound. The two rings are joined with the torsion angles C(3)—N(1)—C(8a)—C(8) and C(5)—N(1)—C(8a)—C(1) being 172.2 (3) and 169.1 (3)°, respectively, so that all the non-H atoms lie close to a plane



(1)

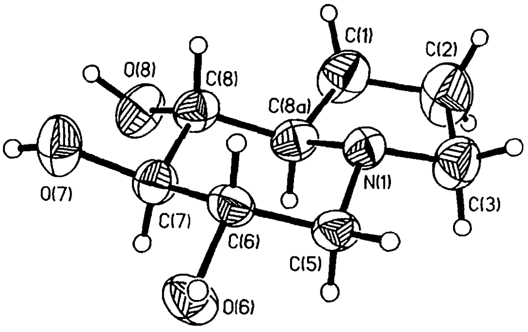


Fig. 1. Perspective view of the 1-deoxycastanospermine molecule with atomic numbering.

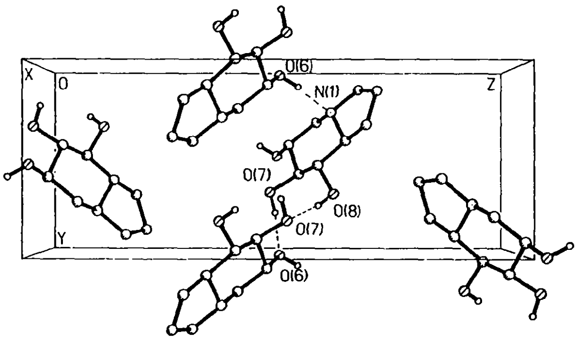


Fig. 2. Packing of the crystal viewed along the *a* axis showing the hydrogen bonds.

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