(+)-Escholinine perchlorate

Marek Nečas,[a]* Jiří Dostál[b] and Jiří Slavík[b]

[a]Department of Inorganic Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic, and [b]Department of Biochemistry, Faculty of Medicine, Masaryk University, Komenského nám. 2, 662 43 Brno, Czech Republic

Correspondence e-mail: man@chemi.muni.cz

(+)-Escholinine perchlorate, $C_{21}H_{26}NO_4^+ \cdot ClO_4^-$, is a quaternary benzyltetrahydroisoquinoline alkaloid isolated from *Eschscholtzia californica*. The partially saturated nitrogen heterocycle has an almost regular half-chair conformation, with the N atom lying 0.666 (3) Å out of the plane of the other atoms. The two methoxy groups lie in the plane of their parent benzene ring. The dihedral angle between the two aromatic rings is 31.44 (7)°.

Comment

(+)-Escholinine, an *N*-methyl derivative of (+)-romneine, is a quaternary benzyltetrahydroisoquinoline alkaloid isolated (as its perchlorate) from *Eschscholtzia californica* Cham. (Papaveraceae) (Slavík & Dolejš, 1973). It is a minor component of the highly polar fraction of alkaloids from this source. Recently, it has been isolated from *Romneya coulteri* Harv. (Valpuesta *et al.*, 1999). The corresponding tertiary base (+)-romneine also occurs in the same plant species (Stermitz *et al.*, 1966).

(I)
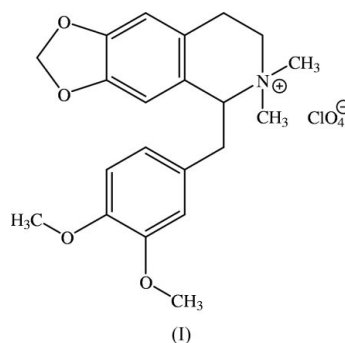
(+)-Escholinine perchlorate, (I), possesses a tetrahydroisoquinoline skeleton with a substituted benzyl group attached to C1 (Fig. 1). All bond lengths and angles are within normal ranges. The bond lengths involving tetravalent nitrogen (N2—C1, N2—C3, N2—C16 and N2—C17) are 1.524 (2), 1.509 (3), 1.488 (3) and 1.496 (3) Å, respectively. These are somewhat longer than the corresponding N—C distances in the tertiary tetrahydroisoquinoline alkaloids egenine and armepavine (Dokurno *et al.*, 1993; Marek *et al.*, 1997). The mean of the bond angles around N2 is 109.5°, appropriate for sp^3 hybridization. The two methoxy groups at C12 and C13 lie in the plane of their parent benzene ring. The partially saturated nitrogen heterocycle has an almost regular half-chair conformation, with atom N2 lying 0.666 (3) Å out of the least-squares plane C1/C8a/C4a/C4/C3. The dihedral angle between the aromatic rings of the isoquinoline moiety and the benzyl group is 31.44 (7)°.

The molecule of (I) contains one chiral centre, atom C1. From previous steric correlations, it is known that dextrorotatory benzyltetrahydroisoquinoline alkaloids have the *S* configuration (Šantavý, 1979; Bentley, 1998). In accordance with previous investigations, and with the refinement of the Flack (1983) parameter, the molecule of escholinine in Fig. 1 is depicted as the *S* enantiomer.

The perchlorate anion is a regular tetrahedron. The mean Cl—O bond length is 1.418 Å. There are no hydrogen bonds and the ions are held together by Coulombic and van der Waals interactions. The isoquinoline rings are stacked in columns parallel to the crystallographic *a* axis.

Experimental

(+)-Escholinine was isolated as a perchlorate salt from the roots of *Eschscholtzia californica* Cham. (Slavík & Dolejš, 1973) and recrystallized from methanol; m.p. 482–483 K, $[\alpha]_D^{25} = +74°$ (0.3 *M* in methanol).

Crystal data

$C_{21}H_{26}NO_4^+ \cdot ClO_4^-$	$D_x = 1.451$ Mg m^{-3}
$M_r = 455.88$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 500
$a = 7.450 (1)$ Å	reflections
$b = 17.010 (3)$ Å	$\theta = 4.5–27.8°$
$c = 9.038 (2)$ Å	$\mu = 0.23$ mm^{-1}
$\beta = 114.32 (3)°$	$T = 120 (2)$ K
$V = 1043.7 (3)$ Å^3	Prism, colourless
$Z = 2$	$0.40 \times 0.40 \times 0.20$ mm

Data collection

Kuma KM-4 CCD diffractometer	$R_{int} = 0.035$
ω scans	$\theta_{max} = 25.0°$
6727 measured reflections	$h = -8 \rightarrow 8$
3144 independent reflections	$k = -20 \rightarrow 19$
3001 reflections with $I > 2\sigma(I)$	$l = -10 \rightarrow 9$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
$wR(F^2) = 0.067$	$\Delta\rho_{min} = -0.20$ e Å^{-3}
$S = 1.04$	Extinction correction: *SHELXTL*
3144 reflections	Extinction coefficient: 0.0106 (15)
281 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	1276 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2$	Flack parameter = $-0.04 (5)$
$+ 0.1452P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Data collection: *Xcalibur* (Oxford Diffraction Ltd, 2001); cell refinement: *Xcalibur*; data reduction: *Xcalibur*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine
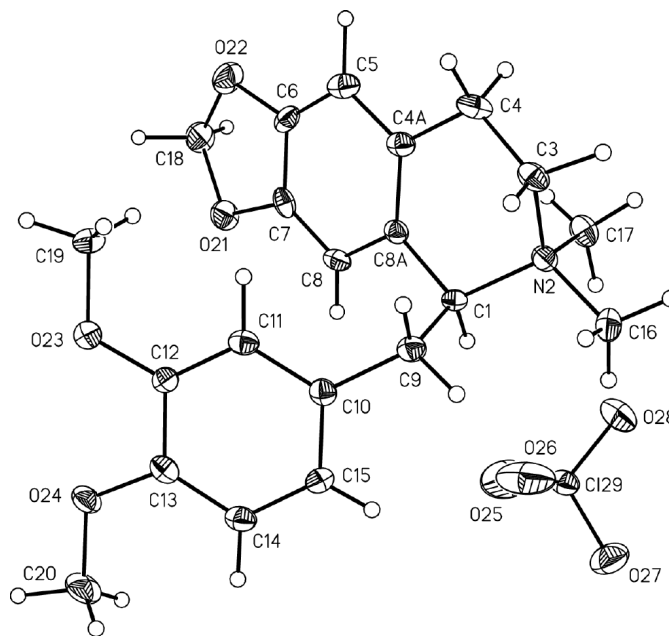
Figure 1
A perspective view of (+)-escholinine perchlorate with the atom numbering. Ellipsoids are drawn at the 50% probability level.

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Bentley, K. W. (1998). *The Isoquinoline Alkaloids*, pp. 33–57. Amsterdam: Harwood Academic Publishers.
Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Dokurno, P., Gdaniec, M., Kosturkiewicz, Z., Matecka, D. & Rozwadowska, M. D. (1993). *Acta Cryst.* C49, 517–519.
Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.
Marek, R., Marek, J., Dostál, J. & Slavík, J. (1997). *Collect. Czech. Chem. Commun.* 62, 1623–1630.
Oxford Diffraction Ltd (2001). *Xcalibur CCD System – CrysAlis Software System*. Version 1.166. Oxford Diffraction Ltd, Oxford, England.
Slavík, J. & Dolejš, L. (1973). *Collect. Czech. Chem. Commun.* 38, 3514–3520.
Stermitz, F. R., Chen, L. & White, J. I. (1966). *Tetrahedron*, 22, 1095–1102.
Šantavý, F. (1979). *The Alkaloids*, Vol. 17, edited by R. H. F. Manske & R. G. A. Rodrigo, pp. 385–544. New York: Academic Press.
Valpuesta, M., Diaz, A. & Suau, R. (1999). *Phytochemistry*, 51, 1157–1160.