

References

- CANTIN, M., XU, Y. C. & DESLONGCHAMPS, P. (1990). *Can. J. Chem.* **68**, 2144–2152.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, edited by J. A. IBERS & W. C. HAMILTON, Table 2.2B, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DROUIN, M., MICHEL, A. G., XU, Y.-C. & DESLONGCHAMPS, P. (1990). *Acta Cryst.* **C46**, 1884–1886.
- GABE, E. J., LEE, F. L. & LE PAGE, Y. (1985). *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 167–174. Oxford: Clarendon Press.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LAMOTHE, S., NDIWAMI, A. & DESLONGCHAMPS, P. (1988). *Tetrahedron Lett.* **29**, 1639–1640.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- MICHEL, A. G., MICHEL-DEWEZ, N. & ROUGHTON, A. L. (1989). *Acta Cryst.* **C45**, 327–329.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1993). **C49**, 517–519

Structure of (\pm)-Egenine

BY P. DOKURNO

Department of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 Gdańsk, Poland

AND M. GDANIEC, Z. KOSTURKIEWICZ, D. MATECKA AND M. D. ROZWADOWSKA

Department of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

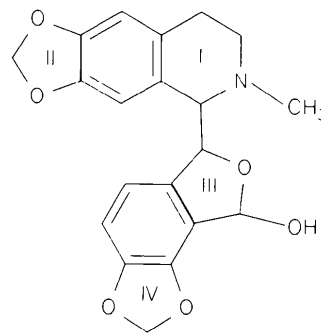
(Received 2 March 1992; accepted 10 July 1992)

Abstract. 6,8-Dihydro-6-(5,6,7,8-tetrahydro-6-methyl-1,3-dioxolo[4,5-g]isoquinolin-5-yl)furo[3,4-*e*]-1,3-benzodioxol-8-ol, $C_{20}H_{19}NO_6$, $M_r = 369.4$, triclinic, $P\bar{1}$, $a = 10.833$ (2), $b = 13.184$ (3), $c = 13.375$ (3) Å, $\alpha = 89.73$ (3), $\beta = 74.52$ (3), $\gamma = 71.95$ (3)°, $V = 1744.0$ (5) Å³, $Z = 4$, $D_x = 1.407$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 8.30$ cm⁻¹, $F(000) = 776$, room temperature, $R = 0.051$ for 3375 observed reflections. The relative configuration of the hemiacetal C atom is established. The heterocyclic fragment of isoquinoline exhibits a half-chair conformation; all five-membered rings show envelope conformations. There is one intramolecular hydrogen bond, closing a seven-membered ring.

Introduction. (+)-Egenine, one of the representatives of the phthalideisoquinoline hemiacetals, was isolated from *Fumaria vaillantii* Loisel (Gözler, Gözler & Shamma, 1983). The molecule has three asymmetric centres [C(1), C(14) and C(16)]. The configuration of C(1) and C(14) has been established on chemical grounds (Gözler, Gözler & Shamma, 1983), yet the stereochemistry around the anomeric centre C(16) was not determined.

We have prepared (\pm)-egenine by Dibal-H reduction of (\pm)-bicuculline (Rozwadowska & Matecka, 1991). The reduction appeared to be a highly stereospecific process leading exclusively to one of the anomeric hemiacetals. We presumed (Rozwadowska & Matecka, 1991) that the anomeric form which is

stabilized by the intramolecular hydrogen bond is formed.



(\pm)-Egenine

Experimental. Crystals (colourless prisms) were obtained from a methanol and chloroform mixture (1:1). The space group was determined from Weissenberg photographs. A crystal of dimensions $0.1 \times 0.15 \times 0.2$ mm was used for measurements on a Syntex $P2_1$ diffractometer, with θ - 2θ scans. Cell parameters were determined from least-squares treatment of the setting angles of 15 reflections with $16 \leq 2\theta \leq 27^\circ$. No absorption or extinction corrections were applied. 4622 reflections with $\sin\theta/\lambda \leq 0.55$ Å⁻¹ were measured in the range $h 0 \rightarrow 14$, $k -11 \rightarrow 11$, $l -14 \rightarrow 14$. Two standard reflections ($\bar{3}\bar{1}2$ and $3\bar{1}1$), recorded every 98 measurements, showed intensity variation of $\pm 6\%$. 3375 reflections were observed with $I \geq 4\sigma(I)$; peak profile analysis was according to

Lehmann & Larsen (1974). The structure was solved by direct methods using the *SHELXS86* (Sheldrick, 1986) program. Full-matrix least-squares refinement [function minimized: $\sum w(F_o - F_c)^2$ with $w^{-1} = \sigma^2(F_c) + 0.00005F_c^2$] used anisotropic displacement parameters for the non-H atoms. Two H(27) atoms, at O(27), were found from a ΔF map, remaining H atoms from standard geometry; isotropic displacement coefficients of H atoms were refined. $R = 0.051$, $wR = 0.056$, $\Delta/\sigma \leq 0.15$, $(\Delta\rho)_{\max} = 0.21$, $(\Delta\rho)_{\min} = -0.20 \text{ e } \text{Å}^{-3}$.

Computer programs used: *SHELXL76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986), *CSU88* (Vičková, 1988) and local programs (Jaskólski, 1982a). Scattering factors used were those stored in *SHELXL76*. Molecular illustrations were drawn using *ORTEPII* (Johnson, 1976).

Discussion. Atomic parameters are given in Table 1 and molecular geometry in Table 2.* The labelling sequence and a view of molecule *A* are presented in Fig. 1. The molecule consists of an isoquinoline fragment with the hydrogenated heterocyclic ring (I) condensed with the 1,3-dioxolo ring (II) and linked with the hemiacetal of phthalide derivative [five-membered ring (III)], also condensed with the 1,3-dioxolo ring (IV). There is one methyl group bonded to N(2), and a hydroxyl group on C(16). There are two independent molecules of egenine in the asymmetric unit.

Bond lengths and angles do not deviate significantly from standard values. Aromatic rings are planar and the normals to their planes form angles of $60.4 (1)^\circ$ in molecule *A* and $66.5 (1)^\circ$ in molecule *B*. Others are puckered showing a half-chair conformation (I), with C(3) below the ring plane (to the phthalide fragment), or an envelope [(II), (III) and (IV)] conformation, with C(12), O(15) and (very slightly) C(24) out of the respective planes. Asymmetry parameters: (I) $\Delta C_{2,3}^{2,3} = 13.26$ (molecule *A*) and 14.26 (molecule *B*); (II) $\Delta C_s^{1,2} = 0.67$ (molecule *A*) and 0.15 (molecule *B*); (III) $\Delta C_s^{1,5} = 3.91$ (molecule *A*) and 1.07 (molecule *B*); (IV) $\Delta C_s^{2,4} = 0.06$ (molecule *A*) and 1.50 (molecule *B*) (Duax & Norton, 1975). The sum of valence angles around N(2) (336.1° in molecule *A* and 335.3° in *B*) shows its sp^3 hybridization, with a lone electron pair participating in an intramolecular hydrogen bond between O(27) and N(2), closing the seven-membered ring [O(27)—H(27) $0.96 (5)$ (molecule *A*) and $1.09 (6)$ Å (molecule

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

$$U_{eq} = (1/3)[U_{11}(a^*a)^2 + U_{22}(b^*b)^2 + U_{33}(c^*c)^2 + 2(U_{12}a^*b^*abc\cos\gamma + U_{13}a^*c^*accos\beta + U_{23}b^*c^*bccos\alpha)].$$

Molecule A	x	y	z	U _{eq}
C(1)	2939 (3)	10948 (3)	9904 (3)	40 (1)
N(2)	1749 (3)	10648 (2)	10466 (2)	44 (1)
C(3)	554 (4)	11135 (3)	10078 (3)	50 (1)
C(4)	133 (4)	12351 (3)	10101 (3)	53 (1)
C(5)	1072 (4)	13773 (3)	9308 (3)	46 (1)
C(6)	2154 (4)	14124 (3)	8942 (3)	48 (1)
C(7)	3454 (4)	13489 (3)	8888 (3)	49 (1)
C(8)	3725 (4)	12473 (3)	9175 (3)	43 (1)
C(9)	2632 (3)	12075 (3)	9557 (3)	38 (1)
C(10)	1318 (3)	12728 (3)	9629 (3)	41 (1)
O(11)	2165 (3)	15108 (2)	8589 (2)	74 (1)
C(12)	3523 (5)	15100 (4)	8413 (6)	109 (2)
O(13)	4346 (3)	14042 (2)	8508 (2)	76 (1)
C(14)	3881 (3)	10102 (3)	9001 (3)	40 (1)
O(15)	4414 (2)	9101 (2)	9419 (2)	48 (1)
C(16)	3729 (4)	8371 (3)	9268 (3)	43 (1)
C(17)	3203 (3)	8778 (3)	8364 (3)	37 (1)
C(18)	2694 (3)	8334 (3)	7706 (3)	40 (1)
C(19)	2234 (3)	8911 (3)	6936 (3)	45 (1)
C(20)	2241 (4)	9942 (3)	6803 (3)	51 (1)
C(21)	2774 (4)	10395 (3)	7457 (3)	46 (1)
C(22)	3244 (3)	9815 (3)	8223 (3)	37 (1)
O(23)	2570 (3)	7332 (2)	7668 (2)	56 (1)
C(24)	2107 (5)	7259 (3)	6770 (3)	64 (1)
O(25)	1797 (3)	8289 (2)	6373 (2)	64 (1)
C(26)	1435 (5)	10880 (4)	11594 (3)	69 (1)
O(27)	2711 (3)	8376 (2)	10173 (2)	53 (1)

Molecule B	x	y	z	U _{eq}
C(1)	6972 (3)	7475 (3)	5024 (3)	42 (1)
N(2)	8194 (3)	6565 (2)	4506 (2)	46 (1)
C(3)	9339 (4)	6456 (3)	4946 (3)	54 (1)
C(4)	9756 (4)	7441 (3)	4945 (3)	55 (1)
C(5)	8786 (4)	9351 (3)	5711 (3)	49 (1)
C(6)	7694 (4)	10252 (3)	6043 (3)	50 (1)
C(7)	6421 (4)	10270 (3)	6052 (3)	49 (1)
C(8)	6164 (4)	9390 (3)	5758 (3)	46 (1)
C(9)	7259 (3)	8444 (3)	5403 (3)	39 (1)
C(10)	8561 (3)	8427 (3)	5377 (3)	41 (1)
O(11)	7671 (3)	11239 (2)	6401 (2)	69 (1)
C(12)	6338 (4)	11937 (4)	6444 (4)	78 (1)
O(13)	5508 (3)	11282 (2)	6418 (2)	72 (1)
C(14)	5981 (4)	7098 (3)	5888 (3)	47 (1)
O(15)	5508 (2)	6357 (2)	5444 (2)	55 (1)
C(16)	6194 (4)	5288 (3)	5631 (3)	52 (1)
C(17)	6659 (3)	5449 (3)	6564 (3)	41 (1)
C(18)	7171 (4)	4761 (3)	7233 (3)	47 (1)
C(19)	7552 (4)	5125 (3)	8030 (3)	53 (1)
C(20)	7463 (4)	6175 (4)	8185 (3)	62 (1)
C(21)	6937 (4)	6893 (3)	7504 (3)	55 (1)
C(22)	6549 (3)	6523 (3)	6715 (3)	42 (1)
O(23)	7412 (3)	3674 (2)	7236 (2)	63 (1)
C(24)	7756 (5)	3400 (4)	8193 (4)	78 (2)
O(25)	8026 (3)	4287 (3)	8593 (2)	74 (1)
C(26)	8596 (6)	6634 (4)	3373 (3)	76 (2)
O(27)	7282 (3)	4787 (2)	4750 (2)	64 (1)

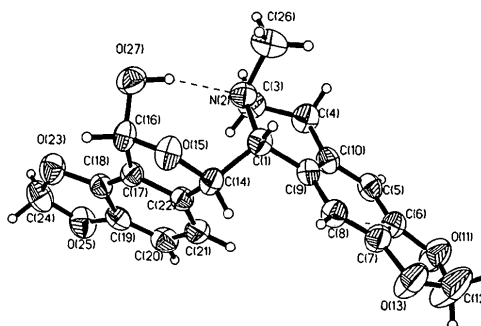


Fig. 1. View of (-)-egenine (molecule *A*).

* Lists of structure factors, anisotropic displacement coefficients and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55586 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1008]

Table 2 *Molecular geometry* (Å, °)

	Molecule A	Molecule B
C(1)—N(2)	1.476 (5)	1.485 (4)
C(1)—C(9)	1.518 (5)	1.524 (6)
C(1)—C(14)	1.547 (5)	1.549 (5)
N(2)—C(3)	1.482 (5)	1.478 (6)
N(2)—C(26)	1.467 (5)	1.471 (5)
C(3)—C(4)	1.523 (5)	1.501 (6)
C(4)—C(10)	1.501 (6)	1.505 (4)
C(5)—C(6)	1.362 (6)	1.364 (5)
C(5)—C(10)	1.408 (6)	1.411 (6)
C(6)—C(7)	1.380 (5)	1.369 (7)
C(6)—O(11)	1.381 (5)	1.379 (5)
C(7)—C(8)	1.356 (5)	1.357 (6)
C(7)—O(13)	1.376 (6)	1.388 (4)
C(8)—C(9)	1.413 (6)	1.406 (4)
C(9)—C(10)	1.395 (4)	1.395 (5)
O(11)—C(12)	1.423 (7)	1.438 (5)
C(12)—O(13)	1.430 (6)	1.433 (7)
C(14)—O(15)	1.442 (5)	1.431 (6)
C(14)—C(22)	1.500 (6)	1.498 (6)
O(15)—C(16)	1.429 (6)	1.431 (4)
C(16)—C(17)	1.499 (6)	1.503 (6)
C(16)—O(27)	1.402 (5)	1.413 (4)
C(17)—C(18)	1.373 (6)	1.370 (6)
C(17)—C(22)	1.392 (6)	1.395 (6)
C(18)—C(19)	1.385 (6)	1.378 (7)
C(18)—O(23)	1.371 (5)	1.375 (5)
C(19)—C(20)	1.372 (6)	1.370 (7)
C(19)—O(25)	1.379 (6)	1.378 (5)
C(20)—C(21)	1.394 (7)	1.409 (6)
C(21)—C(22)	1.387 (6)	1.377 (6)
O(23)—C(24)	1.434 (6)	1.440 (6)
C(24)—O(25)	1.430 (5)	1.429 (7)
O(27)—H(27)	0.96 (5)	1.09 (6)
N(2)—C(1)—C(9)	115.4 (3)	114.8 (3)
N(2)—C(1)—C(14)	111.7 (3)	111.1 (3)
C(9)—C(1)—C(14)	111.9 (3)	112.4 (3)
C(1)—N(2)—C(3)	112.8 (3)	113.1 (3)
C(1)—N(2)—C(26)	111.2 (3)	111.1 (3)
C(3)—N(2)—C(26)	111.8 (3)	111.1 (3)
N(2)—C(3)—C(4)	114.0 (3)	114.7 (3)
C(3)—C(4)—C(10)	111.6 (3)	111.8 (3)
C(6)—C(5)—C(10)	117.8 (4)	117.7 (4)
C(5)—C(6)—C(7)	121.8 (4)	121.7 (4)
C(5)—C(6)—O(11)	128.3 (4)	127.8 (4)
C(7)—C(6)—O(11)	109.9 (3)	110.5 (4)
C(6)—C(7)—C(8)	121.7 (4)	122.2 (4)
C(6)—C(7)—O(13)	109.9 (3)	109.7 (3)
C(8)—C(7)—O(13)	128.4 (4)	128.1 (4)
C(7)—C(8)—C(9)	118.3 (4)	118.2 (4)
C(1)—C(9)—C(8)	118.0 (3)	117.9 (3)
C(1)—C(9)—C(10)	122.3 (3)	122.3 (3)
C(8)—C(9)—C(10)	119.7 (3)	119.8 (4)
C(4)—C(10)—C(5)	118.7 (3)	118.9 (3)
C(4)—C(10)—C(9)	120.6 (3)	120.6 (3)
C(5)—C(10)—C(9)	120.6 (4)	120.5 (4)
C(6)—O(11)—C(12)	105.3 (4)	104.3 (3)
O(11)—C(12)—O(13)	108.7 (4)	107.8 (4)
C(7)—O(13)—C(12)	105.3 (4)	104.5 (3)
C(1)—C(14)—O(15)	109.4 (3)	110.1 (3)
C(1)—C(14)—C(22)	116.6 (3)	116.0 (3)
O(15)—C(14)—C(22)	104.0 (3)	104.9 (3)
C(14)—O(15)—C(16)	110.4 (3)	109.9 (3)
O(15)—C(16)—C(17)	102.7 (3)	103.1 (3)
O(15)—C(16)—O(27)	110.7 (3)	110.2 (3)
C(17)—C(16)—O(27)	113.6 (3)	112.5 (3)
C(16)—C(17)—C(18)	132.4 (4)	132.8 (4)
C(16)—C(17)—C(22)	109.9 (3)	109.6 (3)
C(18)—C(17)—C(22)	117.7 (3)	117.6 (4)
C(17)—C(18)—C(19)	120.5 (4)	120.8 (4)
C(17)—C(18)—O(23)	129.1 (3)	129.0 (4)
C(19)—C(18)—O(23)	110.4 (3)	110.2 (4)
C(18)—C(19)—C(20)	122.4 (4)	122.4 (4)
C(18)—C(19)—O(25)	109.4 (3)	109.9 (4)
C(20)—C(19)—O(25)	128.2 (4)	127.8 (4)
C(19)—C(20)—C(21)	117.6 (4)	117.5 (4)
C(20)—C(21)—C(22)	120.0 (4)	119.7 (4)
C(14)—C(22)—C(17)	107.7 (3)	107.3 (3)
C(14)—C(22)—C(21)	130.5 (4)	130.8 (4)
C(17)—C(22)—C(21)	121.8 (4)	122.0 (4)
C(18)—O(23)—C(24)	105.4 (3)	104.8 (3)
O(23)—C(24)—O(25)	108.4 (3)	107.9 (4)
C(19)—O(25)—C(24)	105.8 (3)	105.3 (4)
C(1)—N(2)—C(3)—C(4)	-56.0 (4)	-55.8 (4)
C(1)—C(9)—C(10)—C(4)	2.6 (6)	1.3 (6)

Table 2. (*cont.*)

	Molecule A	Molecule B
C(1)—C(14)—O(15)—C(16)	103.3 (3)	102.9 (3)
C(1)—C(14)—C(22)—C(21)	71.8 (5)	70.5 (6)
N(2)—C(1)—C(14)—O(15)	-63.5 (4)	-62.9 (4)
N(2)—C(3)—C(4)—C(10)	48.4 (4)	48.3 (5)
C(3)—C(4)—C(10)—C(5)	161.5 (4)	161.9 (4)
C(4)—C(3)—N(2)—C(26)	70.2 (4)	69.9 (4)
C(6)—O(11)—C(12)—O(13)	9.1 (5)	17.4 (4)
C(8)—C(7)—O(13)—C(12)	-175.4 (5)	-170.8 (4)
C(8)—C(9)—C(1)—C(14)	-61.3 (4)	-61.1 (5)
O(11)—C(6)—C(7)—O(13)	0.5 (5)	0.2 (5)
C(14)—O(15)—C(16)—C(17)	23.6 (4)	22.8 (4)
C(14)—O(15)—C(16)—O(27)	-98.1 (3)	-97.5 (4)
C(14)—C(22)—C(17)—C(16)	3.3 (4)	1.0 (4)
C(16)—C(17)—C(22)—C(21)	-178.0 (4)	-178.5 (4)
C(17)—C(18)—O(23)—C(24)	-174.3 (4)	-171.7 (4)
C(18)—C(19)—O(25)—C(24)	-4.7 (4)	-7.5 (5)
O(23)—C(18)—C(19)—O(25)	-0.1 (4)	-1.4 (5)
C(22)—C(14)—C(1)—H(1)	168	171
C(8)—C(9)—C(1)—H(1)	56	56
C(9)—C(1)—C(14)—H(14)	41	45
C(21)—C(22)—C(14)—H(14)	-44	-45
C(22)—C(17)—C(16)—H(16)	-140	-137
C(18)—C(17)—C(16)—H(16)	42	44
C(14)—O(15)—C(16)—H(16)	145	145
C(17)—C(16)—O(27)—H(27)	-65	-72
O(15)—C(16)—O(27)—H(27)	50	43

B); H(27)⋯N(2) 1.92 (5) (*A*) and 1.73 (6) Å (*B*); O(27)⋯N(2) 2.841 (4) (*A*) and 2.799 (4) Å (*B*), O(27)—H(27)⋯N(2) 162 (4) (*A*) and 164 (5)° (*B*)]. The hydrogen-bond ΔH_A parameters, describing the shortening of the H⋯*A* distance with respect to the sum of their van der Waals radii (Jaskólski, 1982*b*), are 23 (molecule *A*) and 31 (molecule *B*). Thus the hydrogen bonds range from medium weak to medium. Four diastereoisomers might occur as products of the reduction reaction (*RSR*, *RSS*, *SRS* and *SRR*), but because of hydrogen-bond formation, only one pair of enantiomers is observed: C(1) *R(S)*, C(14) *S(R)* and C(16) *R(S)*. They are almost mirror images of each other.

There are no unusual intermolecular contacts between molecules.

References

- DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*, Vol. I. New York: Plenum.
- GÖZLER, B., GÖZLER, T. & SHAMMA, M. (1983). *Tetrahedron*, **39**, 577–580.
- JASKÓLSKI, M. (1982*a*). *Abstracts of Fourth Symposium on Organic Crystal Chemistry*, Poznań, September 1982, edited by Z. KAŁUSKI, pp. 70–71. A. Mickiewicz Univ., Poznań, Poland.
- JASKÓLSKI, M. (1982*b*). *Abstracts of Fourth Symposium on Organic Crystal Chemistry*, Poznań, September 1982, edited by Z. KAŁUSKI, pp. 221–245. A. Mickiewicz Univ., Poznań, Poland.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- ROZWADOWSKA, M. D. & MATECKA, D. (1991). *Justus Liebigs Ann. Chem.* pp. 287–289.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1986). *SHELX86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
- VIČKOVIČ, I. (1988). *CSU88*. Program for the calculation and presentation of geometrical parameters in crystal structure analysis. Univ. of Zagreb, Yugoslavia.