H···O and N–H···O hydrogen bonds (Fig. 2, Table 6) forming infinite layers parallel to the *yz* plane at a distance of 10·959 Å.

Both O(7) and O(8) in the carboxyl group are involved in hydrogen bonds: O(*W*)–H···O(8) 2·983(8), N(12)–H···O(8) 2·841(8), and N^+(3)–H···O(7) 2·698 (8) Å. N(3) (carrying a positive charge) in the thiazolidine ring is engaged in one more hydrogen bond of 2·756 (8) Å with a water molecule. The amide O atom is hydrogen-bonded to a water molecule by O(*W*)–H···O(14), 2·775 (8) Å.

The intensities were collected on a Philips PW 1100 diffractometer at the Department of General and Inorganic Chemistry, Faculty of Science, University of Zagreb. The authors thank Magistar Milenko Bruvo for collecting the data, and Drs J. J. Herak, M. Movačević and B. Gašpert for crystals and helpful comments.

References

ABRAHAMSSON, S., CROWFOOT HODGKIN, D. & MASLEN, E. N. (1963). *Biochem. J.* **86**, 514–535.

CLARKE, H. T., JOHNSON, J. R. & ROBINSON, R. (1949). *The Chemistry of Penicillin*. Princeton Univ. Press.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

CROWFOOT, D., BUNN, C. W., ROGERS-LOW, B. W. & TURNER-JONES, A. (1949). *The Chemistry of Penicillin*, pp. 310–358. Princeton Univ. Press.

DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

HERAK, J. J., KOVAČEVIĆ, M. & GAŠPERT, B. (1977). *Croat. Chem. Acta*, **49**, 141–148.

ROBERTSON, J. M. (1972). *Chemical Crystallography. Physical Chemistry, Series One.* Vol. 11, pp. 183–185. London: Butterworths.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J.Chem. Phys.* **42**, 3175–3187.

SWEET, R. M. & DAHL, L. F. (1970). *J. Am. Chem. Soc.* **92**, 5489–5507.

WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

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Crystal Structure of L-Tyrosyl-glycyl-glycine Monohydrate, the N-Terminal Tripeptide of the Enkephalins

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The tripeptide L-tyrosyl-glycyl-glycine, the N-terminal portion of endogenous pentapeptides with opiate activity (the enkephalins), crystallizes from acetic acid/isopropanol solutions as the hydrate ($C_{13}H_{17}N_3O_5.H_2O$). Crystals of the tripeptide are orthorhombic, a = 9·549 (2), b = 18·405 (5), c = 8·012 (1) Å, space group $P2_12_12_1$, with Z = 4. Data were collected on a four-circle diffractometer and the structure was solved by direct methods (R = 0·029). The molecule exists in the crystal as a zwitterion with extensive intermolecular hydrogen bonding. Although no intramolecular hydrogen bonds are present, the molecule assumes a conformation ($\varphi_2 = 81°$, $\psi_2 = 12°$) similar to that of a left-handed α-helix ($\varphi = 57°$, $\psi = 48°$). The average C_α^n–C_α^{n+1} is 3·80 (2) Å.

Introduction

The discovery (Hughes, Smith, Kosterlitz, Fothergill, Morgan & Morris, 1975) of endogenous materials in porcine brain that mimic opiate activity has generated a great deal of interest. These substances, designated enkephalins, were shown to be two pentapeptides: L-Tyr-Gly-Gly-Phe-Met and L-Tyr-Gly-Gly-Phe-Leu. It was further shown by Simantov, Kuhar, Pasternak & Snyder (1976) that these endogenous ligands were competitors for the opiate receptor sites in brain tissue, implicating a structural similarity between enkephalins

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and morphine-like compounds. Most opioid peptides have the same N-terminal residues L-tyrosyl-glycyl and the configuration of the N-terminal tyrosyl moiety has been likened to the phenolic ring and associated ethylamine group found in morphine. Structure–function relations have been investigated with synthetic analogs of the enkephalins (Day, Lujan, Dewey, Harris, Radding & Freer, 1976; Walker, Berntson, Sandman, Coy, Schally & Kastin, 1977) and models of the active conformation of enkephalins have been proposed based on theoretical arguments (Bradbury, Smyth & Snell, 1976; Isogai, Nemethy & Scheraga, 1977; Goldstein, Goldstein & Cox, 1975) and NMR investigations (Bleich, Cutnell, Day, Freer, Glasel & McKelvy, 1976; Jones, Gibbons & Garsky, 1976; Garbay-Jaureguiberry, Roques, Oberlin, Anteunis & Lala, 1976; Roques, Garbay-Jaureguiberry, Oberlin, Anteunis & Lala, 1976). These studies generally suggested a β-bend structure stabilized by intramolecular hydrogen bonds.

This paper describes the structure of the N-terminal tripeptide, L-tyrosyl-glycyl-glycine, of the enkephalins. It is the first of a series on these peptides to elucidate the solid-state conformations of endogenous opiates and their analogs. This information will be used to study possible structural analogy between two seemingly different classes of compounds, the rigid opiates and the flexible peptides of the enkephalins. Such comparisons could assist in the design of an effective analgesic lacking the addictive properties of morphine and the opiates.

Experimental

The tripeptide L-Tyr-Gly-Gly was purchased from US Biochemicals. Crystals were grown from 50% glacial acetic acid solutions containing 10 mg ml^{-1} of tripeptide equilibrated *via* the vapor phase against absolute isopropanol. The space group was determined from precession photographs which revealed systematic absences for odd-indexed *h*00, 0*k*0, and 00*l* reflections. Lattice constants were obtained from the least-squares refinement of setting angles of 15 autocentered reflections.

Intensity data were collected from a single crystal (0·5 × 0·4 × 0·1 mm) under a cool nitrogen stream (−35°C) with a Syntex $P2_1$ auto-diffractometer, equipped with a graphite monochromator, and Mo $K\alpha$ radiation. All unique reflections with $4° \leq \theta \leq 52°$ (corresponding to a minimum interplanar spacing of 0·81 Å) were measured with the ω-scan technique. Standard reflections measured at regular intervals indicated good stability of crystal and equipment. The intensities were corrected for background and Lorentz–polarization factors. No absorption corrections were needed because of the small size of the crystal and the value of the absorption coefficient (crystal data are summarized in Table 1). Of the 1607 reflections measured, 1385 had $I \geq 2{\cdot}5\sigma(I)$ and were considered to be observed. The technique and computer programs used are further documented in Riley & Davis (1975).

Table 1. *Crystal data*

Formula $C_{13}H_{17}N_3O_5.H_2O$	Space group $P2_12_12_1$
$M_r = 313{\cdot}3$	$D_o = 1{\cdot}475$ g cm^{-3}
$a = 9{\cdot}549$ (2) Å	$D_c = 1{\cdot}477$
$b = 18{\cdot}405$ (5)	$F(000) = 1252$ e
$c = 8{\cdot}012$ (1)	λ(Mo $K\alpha$) = 0·7107 Å
$V = 1408{\cdot}1$ Å^3	μ(Mo $K\alpha$) = 1·27 cm^{-1}
$Z = 4$	

Solution and refinement of structure

The structure was solved by the multiple-solution tangent formula program *MULTAN* (Germain, Main & Woolfson, 1971) with the 288 largest E values ($E \geq 1{\cdot}3$). Only the 406 reflection was fixed by the Σ_1 relation. The origin was fixed by assigning a phase of 90° to reflections 5,12,0, 105 and 0,13,6, while the 724 reflection was used to fix the enantiomorph. Phase assignments to reflections 724 and 150 were used to generate four basis sets. One phase set gave a figure of merit sixfold higher than any other and produced an E map that clearly revealed the entire peptide structure and another peak later determined to represent an O of a water molecule. Three spurious peaks, all less than half the size of any of the others, were ignored.

Table 2. *Positional parameters* (×10^4) *for* L-*Tyr-Gly-Gly monohydrate*

Estimated standard deviation of last digit is given in parentheses.

	x	*y*	*z*
O(3)	9957 (2)	6175 (1)	2189 (2)
C(3)	8810 (2)	6137 (1)	1452 (2)
O′(3)	8575 (2)	6333 (1)	−26 (2)
C(3*A*)	7570 (3)	5875 (2)	2494 (3)
N(3)	6469 (2)	5518 (1)	1560 (3)
C(2)	5256 (2)	5825 (1)	1179 (3)
O(2)	4982 (2)	6472 (1)	1482 (2)
C(2*A*)	4177 (3)	5352 (1)	299 (3)
N(2)	4495 (2)	4579 (1)	276 (3)
C(1)	4208 (2)	4178 (1)	1629 (3)
O(1)	3847 (2)	4433 (1)	2967 (2)
C(1*A*)	4334 (3)	3356 (1)	1385 (3)
N(1)	4392 (2)	3018 (1)	3069 (3)
C(1*B*)	3093 (3)	3061 (1)	358 (3)
C(*R*1)	1677 (3)	3339 (1)	878 (3)
C(*R*2)	859 (3)	2976 (1)	2044 (3)
C(*R*3)	−448 (3)	3226 (1)	2511 (3)
C(*R*4)	−954 (2)	3863 (1)	1833 (3)
C(*R*5)	−158 (3)	4246 (1)	686 (3)
C(*R*6)	1139 (3)	3980 (1)	207 (3)
O(*R*)	−2253 (2)	4133 (1)	2247 (3)
O(*W*)	2267 (2)	6895 (1)	791 (3)

Table 3. *Coordinates* ($\times 10^3$), *isotropic thermal parameters* (Å^2) *and bond distances* (Å) *for hydrogen atoms*

Estimated standard deviation of last digit is given in parentheses.

	x	*y*	*z*	*B*	C,N,O–H
H(C3*A*)	724 (3)	632 (2)	307 (4)	3·5 (7)	0·99 (5)
H′(C3*A*)	794 (3)	554 (1)	330 (4)	3·2 (7)	0·96 (4)
H(N3)	661 (3)	506 (2)	140 (3)	3·3 (7)	0·86 (4)
H(C2*A*)	408 (3)	553 (2)	−85 (4)	4·1 (7)	0·98 (5)
H′(C2*A*)	328 (3)	544 (1)	84 (3)	3·1 (7)	1·02 (4)
H(N2)	474 (3)	439 (2)	−66 (4)	4·3 (7)	0·86 (5)
H(C1*A*)	519 (3)	325 (1)	83 (3)	2·3 (7)	0·95 (4)
H(N1)	450 (3)	247 (2)	302 (3)	3·9 (7)	1·02 (4)
H′(N1)	358 (3)	309 (2)	370 (4)	3·7 (7)	0·94 (5)
H″(N1)	520 (3)	323 (2)	385 (4)	4·2 (7)	1·07 (5)
H(C1*B*)	312 (2)	253 (1)	39 (3)	2·2 (7)	0·98 (3)
H′(C1*B*)	326 (3)	317 (1)	−79 (3)	3·1 (7)	0·96 (4)
H(C*R*2)	120 (2)	254 (1)	252 (3)	2·1 (7)	0·95 (3)
H(C*R*3)	−98 (2)	297 (1)	329 (3)	1·9 (7)	0·93 (3)
H(C*R*5)	−54 (2)	470 (1)	28 (3)	2·3 (7)	0·97 (3)
H(C*R*6)	171 (3)	426 (1)	−62 (3)	3·1 (7)	1·00 (4)
H(O*R*)	−253 (4)	396 (2)	313 (5)	7·2 (7)	0·82 (6)
H(O*W*)	317 (4)	674 (2)	107 (4)	5·4 (7)	0·94 (5)
H′(O*W*)	164 (4)	662 (2)	125 (4)	5·0 (7)	0·87 (5)

The peptide model was refined minimizing $\Sigma w[|F_o| - (1/k)|F_c|]^2$ by least-squares methods using weights proportional to $1/\sigma^2$. $R_w = \{\Sigma w[|F_o| - (1/k)|F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, $R = \Sigma[|F_o| - (1/k)|F_c|]/\Sigma|F_o|$. Full-matrix isotropic refinement converged at $R_w = 0{\cdot}079$. One anisotropic refinement cycle lowered this to $R_w = 0{\cdot}062$. A subsequent difference map and calculations of ideal positions allowed reasonable placement of all the H atoms, and refinement of these positions gave $R_w = 0{\cdot}041$. Two final cycles of anisotropic refinement of all non-hydrogen atoms gave a final $R_w = R = 0{\cdot}029$ for observed reflections and $R_w = 0{\cdot}030$, $R = 0{\cdot}038$ for all reflections. A final difference electron density map showed no density greater than 0·08 e Å^{-3}. The final positional and H atom isotropic thermal parameters are given in Tables 2 and 3.*

Results

A stereodrawing of the tripeptide, produced by C. K. Johnson's *ORTEP* program, is shown in Fig. 1. Bond lengths and bond angles for all non-hydrogen atoms are reported in Fig. 2. The average e.s.d. in bond length is 0·003 Å; the average e.s.d. in bond angle is 0·3°.

The torsion angles of the tripeptide, given in accordance with the IUPAC–IUB Commission on Biochemical Nomenclature (1971) recommendation, are shown in Table 4. The value of ω_1 (170°) for the tyrosyl–glycyl peptide bond indicates a substantial degree of non-planarity. The deviations from the least-squares plane through the peptide bond are 0·053, −0·084 and 0·068 Å for C(1*A*), N(2) and C(2*A*), respectively. The corresponding deviations for C(2*A*), N(3) and C(3*A*) are −0·019, 0·038 and −0·028.* The Tyr–Gly peptide bond is obviously less planar than the Gly–Gly peptide bond, yet both agree reasonably well in terms of angles and distances with standard values (Pauling & Corey, 1953; Marsh & Donohue, 1967) of a peptide bond in the extended conformation. The

* Lists of structure factors, anisotropic thermal parameters, and a table of least-squares planes and atomic deviations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33194 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

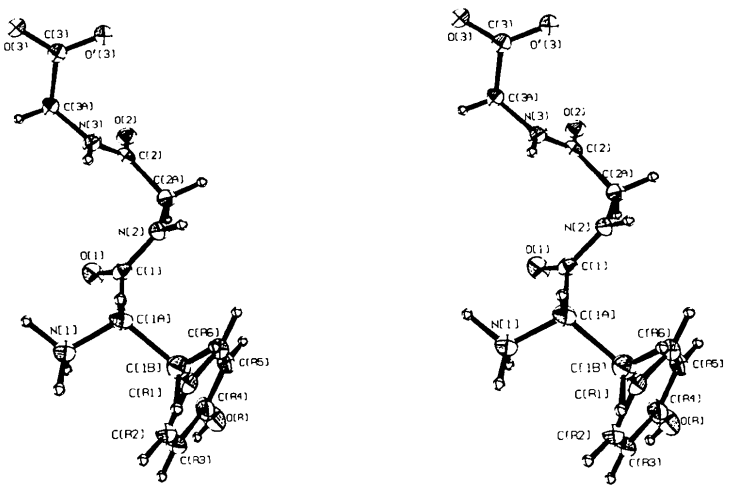

Fig. 1. A stereoview of L-Tyr-Gly-Gly. Ellipsoids of 50% probability are shown. Hydrogen temperature factors are set at $B = 0{\cdot}5$ Å^2 for clarity.

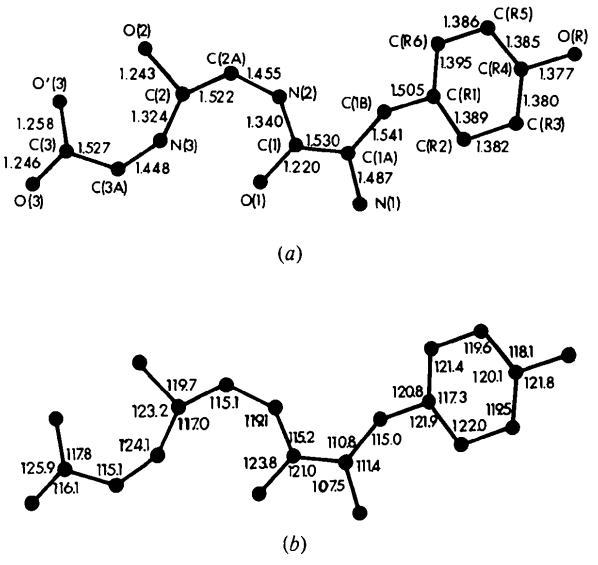

Fig. 2. Molecular dimensions of L-Tyr-Gly-Gly. (*a*) Bond lengths (Å). (*b*) Valence angles (°).

Table 4. *Conformational angles* (°)

[N(1)–C(1*A*)–C(1)–N(2)]	$\psi_1 =$ 164
[C(1*A*)–C(1)–N(2)–C(2*A*)]	$\omega_1 =$ 170
[N(1)–C(1*A*)–C(1*B*)–C(*R*1)]	$\chi_1 =$ 74
[C(1*A*)–C(1*B*)–C(*R*1)–C(*R*2)]	$\chi_2 =$ −91
[C(1)–N(2)–C(2*A*)–C(2)]	$\varphi_2 =$ 81
[N(2)–C(2*A*)–C(2)–N(3)]	$\psi_2 =$ 12
[C(2*A*)–C(2)–N(3)–C(3*A*)]	$\omega_2 =$ −176
[C(2)–N(3)–C(3*A*)–C(3)]	$\varphi_3 =$ −104
[N(3)–C(3*A*)–C(3)–O(3)]	$\psi_T =$ −153

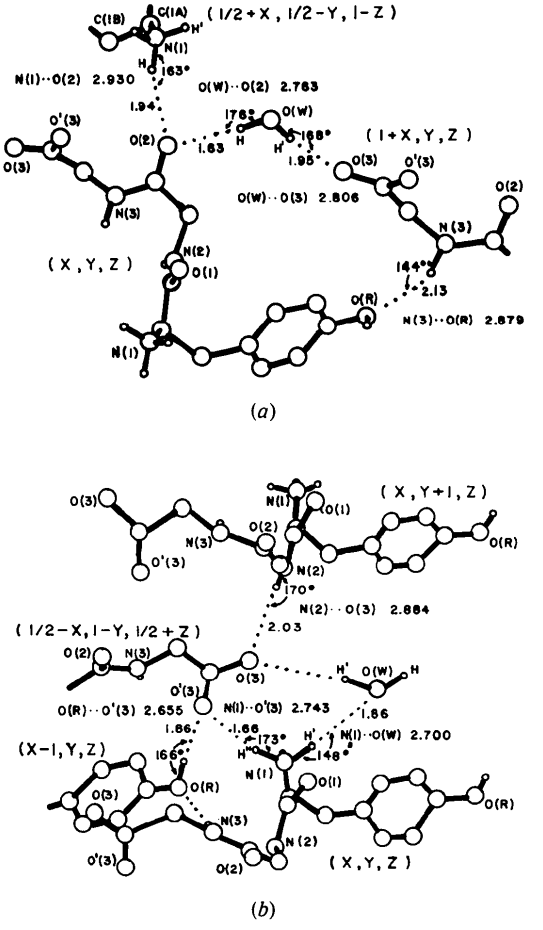

Fig. 3. Hydrogen-bond structure in the crystal structure of L-Tyr-Gly-Gly. (*a*) Chains of translationally related neighbors. (*b*) Interactions about the charged groups. E.s.d.'s are 0·003, 0·03 Å and 2·5° in donor–acceptor distances, hydrogen–acceptor distances and donor–hydrogen–acceptor angles respectively.

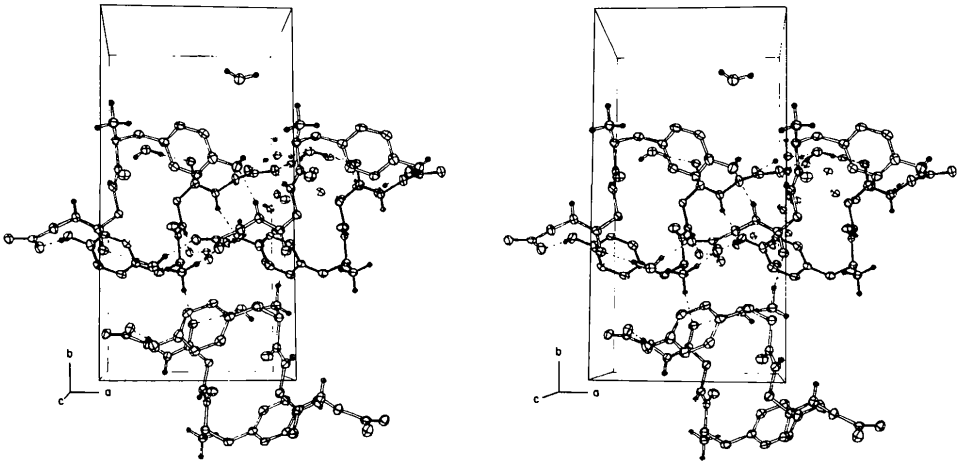

Fig. 4. Hydrogen bonds (dashed lines) and crystal packing in the structure of L-Tyr-Gly-Gly.

average peptide bond length is 1·332 (3) Å. The C_α^n–C_α^{n+1} distances are 3·778 and 3·811 Å for C(1*A*)–C(2*A*) and C(2*A*)–C(3*A*), respectively. The tyrosyl ring is planar, with all C atoms deviating less than 0·01 Å from their mean plane. O(*R*) lies 0·025 Å out of this plane.

No intramolecular hydrogen bonds were found, although the conformation of the tripeptide somewhat resembles a left-handed α-helix, with φ_2, ψ_2 of 81, 12°. The standard φ, ψ values for the left-handed α-helix are 57, 48° (Ramachandran & Sasisekharan, 1968). Tight packing in the crystalline structure is exemplified by the relatively high value for the calculated crystal density, 1·48 g cm^{-3}. Every H in the molecule capable of forming a hydrogen bond does so. The tyrosyl carbonyl O is the only heteroatom not involved in the hydrogen-bonding scheme. Each molecule forms hydrogen-bonded chains with translationally related neighbors, O(3)···H′(*W*)–O(*W*)–H(*W*)···O(2) and N(3)–H···O(*R*). These chains are cross-linked *via* symmetry-related molecules through the extensive interactions of the protonated N(1) and the O(3), O′(3) carboxyl group. The geometry of these chains is represented in Figs. 3 and 4, which give the hydrogen-bond distances and angles and illustrate the crystal packing.

Discussion

All endogenous opioid peptides have the same N-terminal residues L-Tyr-Gly. Arguments for the structural analogy between morphine and the enkephalins have concentrated on the phenol ring linked to an ethylamine moiety. In the enkephalins this represents the 'tyramine' portion of the N-terminal tyrosine residue. While the absolute stereochemistry of the L-tyrosyl α-C is as required for morphine-like activity, the tripeptide L-Tyr-Gly-Gly has not been shown to act either analgesically or in a competitive manner towards opiates in several assay systems (Day, Lujan, Dewey, Harris, Radding & Freer, 1976; Buscher, Hill, Romer, Cardinaux, Closse, Hauser & Pless, 1976). This may imply a necessity for the presence of the next amino acid in the sequence, or the lack of activity might be due to the inability of the receptor site to tolerate a negative charge at the position of the glycyl carboxyl group. Physiological testing of the amidated tripeptide would clarify this point.

Horn & Rodgers (1976) have attempted to deduce information about the 'tyramine' moiety of enkephalins by documenting the spatial relations found in X-ray studies of the corresponding fragment of several conformationally restricted opiate agonists and antagonists. These molecules have a distance of 6·8–7·0 Å from the phenolic OH group to the ionizable amino group coupled with a spatial orientation so as to place this amino N 1·2 Å normal to the plane of the phenolic ring. The distance between the phenolic OH and the N-terminus of the tripeptide shown in Fig. 1 is 6·72 Å. However, the N-terminal N is 2·2 Å above the plane of the aromatic ring system compared with 1·2 Å in the opiates. Thus, there are appreciable differences between this tripeptide and the 'average opiate' in the relative positions of the tyrosyl α-C substituents.

Isogai, Nemethy & Scheraga (1977) reported many compact conformations for the enkephalins of comparable energy, the lowest of which is characterized by a β-bend involving the last four residues which is further stabilized by an additional intramolecular hydrogen bond involving the hydroxyl of the Tyr side chain and the carbonyl O of 3-Gly or 4-Phe. The intramolecular hydrogen bond between the hydroxyl of the tyrosyl side chain and the carbonyl oxygen of the terminal glycine does not exist in this crystal structure although an intermolecular hydrogen bond involving these residues does stabilize the crystal structure. Thus it would appear that for the tripeptide, the crystal packing forces have selected a conformation for the 'tyramine' portion of the enkephalins different from what might be expected for the opiate receptor.

Although this structure cannot provide any definitive insight on the conformation of the enkephalins, it does illustrate the structural features of small peptides including the ability of glycyl peptide bonds to bend sharply. The general applicability of protein folding rules has not been extensively tested on small peptides. Only one crystallographic study (Ueki, Bando, Ashida & Kakudo, 1971) on a series of molecules representing a growing, linear peptide chain has been reported.

Work is in progress on other peptides in this series, including the methionine and leucine enkephalins and the tetrapeptide L-Tyr-Gly-Gly-Phe. In addition to providing information on the structural analogy between the opiates and the enkephalins, these studies will generate structural data on a growing polypeptide chain. The conformational changes observed will help document standard allowed conformations and illustrate factors influencing the folding of small peptides.

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References

BLEICH, H. E., CUTNELL, J. D., DAY, A. R., FREER, R. J., GLASEL, J. A. & MCKELVY, J. F. (1976). *Proc. Natl Acad. Sci. USA*, **73**, 2589–2593.

BRADBURY, A. F., SMYTH, D. G. & SNELL, C. R. (1976). *Nature (London)*, **260**, 165–166.

BUSCHER, H. H., HILL, R. C., ROMER, D., CARDINAUX, F., CLOSSE, A., HAUSER, D. & PLESS, J. (1976). *Nature (London)*, **261**, 423–425.
DAY, A. R., LUJAN, M., DEWEY, W. L., HARRIS, L. S., RADDING, J. A. & FREER, R. J. (1976). *Res. Commun. Chem. Pathol. Pharmacol.* **14**, 597–603.
GARBAY-JAUREGUIBERRY, C., ROQUES, B. P., OBERLIN, R., ANTEUNIS, M. & LALA, A. K. (1976). *Biochem. Biophys. Res. Commun.* **71**, 558–565.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
GOLDSTEIN, A., GOLDSTEIN, J. S. & COX, B. M. (1975). *Life Sci.* **17**, 1643–1654.
HORN, A. S. & RODGERS, J. R. (1976). *Nature (London)*, **260**, 795–797.
HUGHES, J., SMITH, T. W., KOSTERLITZ, H. W., FOTHERGILL, L. A., MORGAN, B. A. & MORRIS, H. R. (1975). *Nature (London)*, **258**, 577–579.
ISOGAI, Y., NEMETHY, G. & SCHERAGA, H. A. (1977). *Proc. Natl Acad. Sci. USA*, **74**, 414–418.
IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1971). *Biochem. J.* **121**, 577–585.
JONES, C. R., GIBBONS, W. A. & GARSKY, V. (1976). *Nature (London)*, **262**, 779–782.
MARSH, R. E. & DONOHUE, J. (1967). *Adv. Protein Chem.* **22**, 235–256.
PAULING, L. & COREY, R. B. (1953). *Proc. R. Soc. London, Ser. B*, **141**, 21–33.
RAMACHANDRAN, G. N. & SASISEKHARAN, V. (1968). *Adv. Protein Chem.* **23**, 283–438.
RILEY, P. E. & DAVIS, R. E. (1975). *Inorg. Chem.* **14**, 2507–2513.
ROQUES, B. P., GARBAY-JAUREGUIBERRY, C., OBERLIN, R., ANTEUNIS, M. & LALA, A. K. (1976). *Nature (London)*, **262**, 778–779.
SIMANTOV, R., KUHAR, M. J., PASTERNAK, G. W. & SNYDER, S. H. (1976). *Brain Res.* **106**, 189–197.
UEKI, T., BANDO, S., ASHIDA, T. & KAKUDO, M. (1971). *Acta Cryst.* B**27**, 2219–2231.
WALKER, J. M., BERNTSON, G. G., SANDMAN, C. A., COY, D. H., SCHALLY, A. V. & KASTIN, A. J. (1977). *Science*, **196**, 85–87.

Acta Cryst. (1978). B**34**, 1280–1283

Structure Cristalline du Sulfate d'*o*-Phénanthroline, $C_{12}H_8N_2.H_2SO_4$

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Crystals of $C_{12}H_8N_2.H_2SO_4$ are monoclinic, space group $P2_1/b$; $a = 7{\cdot}873\ (4)$, $b = 8{\cdot}120\ (4)$, $c = 18{\cdot}36\ (1)$ Å, $\gamma = 92{\cdot}49\ (5)°$; $Z = 4$. The structure has been determined by direct methods and refined by least-squares procedures to $R = 0{\cdot}037$ for 1953 independent reflections recorded with an automatic single-crystal diffractometer. Phenanthroline and sulphate groups alternate in layers.

Introduction

Le sulfate d'*o*-phénanthroline $C_{12}H_8N_2.H_2SO_4$ a été préparé par action de l'acide sulfurique en excès sur l'*o*-phénanthroline. Le monocristal choisi pour effectuer l'étude structurale peut, en première approximation, être assimilé à un prisme droit à base carrée. Il mesure environ $400 \times 400 \times 380\ \mu$m.

Les diagrammes de Weissenberg, réalisés en l'irradiant avec le rayonnement Cu $K\alpha$, ont permis de connaître la symétrie du réseau et les dimensions de la maille. Les dimensions indiquées ci-après ont été obtenues lors des mesures d'intensité avec un diffractomètre automatique Enraf–Nonius CAD-4 fonctionnant avec le rayonnement Mo $K\alpha$ isolé par un monochromateur. Leur détermination a fait intervenir les données angulaires de 15 réflexions.

Données cristallographiques

Le sulfate d'*o*-phénanthroline cristallise dans le système monoclinique. Les extinctions systématiques observées sont celles du groupe spatial $P2_1/b$. Les paramètres cristallins ont les valeurs suivantes: $a = 7{,}873\ (4)$, $b = 8{,}120\ (4)$, $c = 18{,}36\ (1)$ Å et $\gamma = 92{,}49\ (5)°$. Ces valeurs sont compatibles avec la présence de quatre unités formulaires par maille. En effet, dans cette hypothèse, la masse volumique calculée ($\mu_c = 1{,}58$ g cm^{-3}) est voisine de la masse volumique mesurée à partir de monocristaux ($\mu_m = 1{,}61$ g cm^{-3}).

Les mesures d'intensité concernent les réflexions pour lesquelles $0 \le \theta \le 26°$; $-9 \le h \le 9$; $0 \le k \le 10$ et $0 \le l \le 22$. Sur 2456 réflexions mesurées, 1953 ont été conservées pour l'affinement de la structure. Le critère de sélection retenu s'exprime par la relation $I > 2\sigma(I)$.