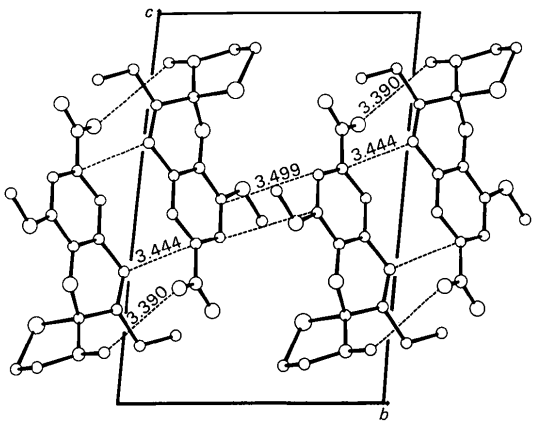

Fig. 2. Molecular packing of the title compound viewed along **a**. (Distances in Å.)

der Waals contact, 3·499 (3) Å, is between C(7) and C(8). The molecular stacks are further cross-linked through short contacts: O(2)···C(9^{i}) 3·255 (3), C(9)···C(9^{i}) 3·733 (4), C(4)···C(10′^{ii}) 3·541 (4) Å; (i) and (ii) correspond to symmetry positions $-x$, $1-y$, $1-z$ and $1+x, y, z$, respectively.

H(5) is involved in short intra- and intermolecular contacts to O(4). The geometry of this weak asymmetrical bifurcated interaction is:

	d (Å)	d (Å)	∠ (°)	∠ (°)
			C(5)–H(5)···	O(4)···H(5)···
	C(5)–H(5)	O(4)···H(5)	O(4)	O(4^{iii})
C(5)–H(5)···O(4)	0·98 (3)	2·37 (3)	100 (2)	
C(5)–H(5)···O(4^{iii})		2·47 (3)	146 (2)	113 (1)

(iii) refers to symmetry position $2-x, -y, 1-z$.

We are grateful to Dr D. White, who kindly provided a copy of his 'ring puckering coordinates' program.

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Structure of *cyclo*(-L-Leucyl-L-tyrosyl-) Monohydrate, $C_{15}H_{20}N_2O_3.H_2O$

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Abstract. $M_r = 294·3$, monoclinic, $P2_1$, $a = 8·883$ (5), $b = 6·105$ (3), $c = 14·582$ (5) Å, $\beta = 99·53$ (4)°, $U = 779·9$ Å^3, $Z = 2$, $D_m = 1·25$, $D_x = 1·25$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·666$ mm^{-1}, $F(000) = 316$, room temperature, $R = 0·075$ for 1147 significant reflections. One of the *cis* peptide units shows significant non-planarity with $\omega = -11·7$ (10)°, the other is planar with $\omega = -2·8$ (10)°. The diketopiperazine ring

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takes a boat form. The leucyl side chain is in an extended conformation [$\chi^2 = 173{\cdot}7\ (7)°$]; the tyrosyl residue shows a folded geometry [$\chi^1 = 59{\cdot}5\ (7)°$]. χ^2 of the tyrosyl side chain is 98·4 (8)°.

Introduction. Tyrosyl-containing diketopiperazines studied so far, *viz* *cyclo*(-Gly-L-Tyr-) and *cyclo*-(-L-Ser-L-Tyr-) (Lin & Webb, 1973), are found to be in a folded conformation. NMR studies (Kopple & Marr, 1967) had indicated that this folded form is favoured over other possible conformations of the arylmethyl side chain by an enthalpy change averaging 12·6 kJ mol^{-1}, this resulting from a direct rather than solvent-mediated interaction between the two rings. It is of interest to see how this conformation is affected by the substitution of different amino acid residues. The leucyl side chain is of particular interest, as many diketopiperazines containing this residue have been found to be the factors causing bitterness. Minamiura, Mutsumara & Yamamoto (1972) isolated the bitter factor from caseine hydrolate by bacterial proteinase in a study of the bitterness of cheese. Shiba, Uratani, Kubota & Sumi (1981) found that the bitter factor is *cyclo*(-L-Leu-L-Trp-); other leucyl-containing bitter diketopeperazines are *cyclo*(-L-Leu-L-Leu-) and *cyclo*-(-L-Leu-Gly-) (Shiba & Nunami, 1974). The structure of *cyclo*(-L-leucyl-L-tyrosyl-) is reported here.

Experimental. Crystals grown by diffusion of water into saturated Me_2SO solution. D_m by flotation is CCl_4/hexane. Space group and cell parameters determined by rotation and Weissenberg methods; cell dimensions refined by least squares using 25 high-angle reflections on a Nonius CAD-4 diffractometer. Intensity data collected on the diffractometer with ω–2θ scans using monochromated Cu $K\alpha$ radiation; crystal 0·08 × 0·10 × 1·88 mm; $\theta_{max} = 60{\cdot}2°$. Two standard reflections monitored at regular intervals, crystal stable to X-rays. Intensities corrected for polarization and Lorentz factors. No absorption correction. Of 1214 unique reflections measured, 1147 considered significant ($|F| \geq 2\sigma|F|$). Index range: h ±9, k 0/6, l 0/16. Structure solved using *MULTAN*80 (Germain, Main & Woolfson, 1971; Main, 1980, private communcation). The E map calculated with the phases corresponding to the best set revealed 18 out of 20 non-H atoms. Subsequent difference maps revealed the remaining non-H atoms as well as the solvent water molecule. Full-matrix least-squares refinement on F (*SHELX*76; Sheldrick, 1976); anisotropic thermal parameters for non-hydrogen atoms; all H atoms, including those of the water molecule, located from a difference map; refinement (including H atoms) converged at R = 0·075; H atoms assigned isotropic thermal parameter U = 0·050 Å^2 and not refined; $w = 1/\sigma^2(|F|)$; wR = 0·089. In final cycle $\Delta/\sigma < 0{\cdot}01$. $\Delta\rho$ in final difference map within +0·4 and −0·5 e Å^{-3}.

Discussion. Final parameters are listed in Table 1.* Fig. 1 shows the *cyclo*(-L-Leu-L-Tyr-) monohydrate molecule with the numbering scheme.

Of the two *cis* peptide units present in the structure one is planar with ω = [C(3)–N(2)–C(2)–C(4)] = −2·8 (10)°; the other is significantly non-planar with ω = [C(3)–C(1)–N(1)–C(4)] = −11·7 (10)°. Non-planarity to such an extent has been observed in only a few diketopiperazines studied so far: *cyclo*(-L-Cys-)$_2$ −10, −16° (Lu & Kartha, 1973); *cyclo*(-L-Cys-)$_2$–

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, bond lengths and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39627 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* (×10^4) *and equivalent isotropic temperature factors of non*-H *atoms with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
O(1)	10130 (6)	6338	4004 (3)	0·037 (3)
O(2)	7600 (5)	−754 (9)	2255 (3)	0·031 (3)
O(3)	14187 (5)	4521 (11)	936 (3)	0·039 (3)
N(1)	8305 (6)	4852 (11)	2925 (4)	0·026 (3)
N(2)	9410 (6)	737 (10)	3331 (4)	0·025 (3)
C(1)	9582 (8)	4743 (13)	3574 (4)	0·026 (4)
C(2)	8246 (7)	882 (13)	2640 (4)	0·023 (3)
C(3)	10334 (8)	2558 (13)	3796 (4)	0·025 (4)
C(4)	7706 (7)	3111 (12)	2284 (5)	0·026 (4)
C(5)	7992 (7)	3582 (13)	1301 (4)	0·026 (3)
C(6)	9651 (7)	3826 (12)	1222 (4)	0·020 (3)
C(7)	10389 (8)	5836 (12)	1411 (4)	0·026 (4)
C(8)	11916 (8)	6082 (13)	1343 (4)	0·027 (3)
C(9)	12700 (7)	4356 (14)	1031 (4)	0·029 (4)
C(10)	11992 (8)	2338 (12)	846 (4)	0·027 (4)
C(11)	10467 (8)	2111 (12)	929 (4)	0·026 (4)
C(12)	11919 (8)	2611 (14)	3529 (4)	0·031 (4)
C(13)	12812 (8)	462 (14)	3709 (5)	0·038 (4)
C(14)	14294 (9)	580 (20)	3327 (6)	0·063 (6)
C(15)	13143 (10)	−188 (20)	4710 (6)	0·070 (6)
*W*O	14852 (5)	3567 (10)	−883 (3)	0·039 (3)

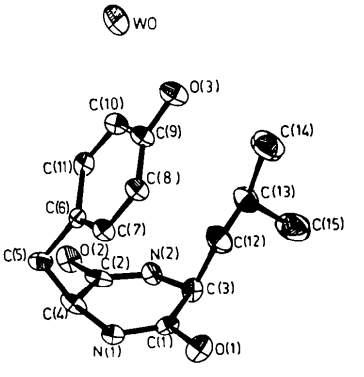


Fig. 1. A diagram of the molecule showing the thermal ellipsoids drawn at the 50% probability level.

acetic acid −14, −17° (Mez, 1974); *cyclo*(-*N*-Me-L-Val-*N*-Me-D-Val-) −19, 19° (Benedetti, Marsh & Goodman, 1976); *cyclo*(-*N*-Me-L-Phe-*N*-Me-D-Phe-) −14, 14° (Benedetti *et al.*, 1976).

The tyrosyl residue is in a folded conformation with the aromatic ring facing the diketopiperazine ring (Fig. 1), a feature found in all diketopiperazines containing this residue. The occurrence of the folded conformation in all three tyrosyl-containing diketopiperazines so far studied crystallographically, independent of the nature or the conformation of the side chain at the other C^{α} atom, seems to suggest that the attractive force between the two rings which stabilizes this conformation may play an important role in molecules of biological interest.

The dihedral angle χ^2 about the C^{α}–C^{β} bond, *i.e.* N(1)–C(4) C(5)–C(6), is 59·5 (7)°. This value is close to that (55°) found in *cyclo*(-Gly-L-Tyr-) and *cyclo*(-L-Ser-L-Tyr-) (Lin & Webb, 1973).

The dihedral angle χ^2 about the C^{β}–C^{γ} bond, *i.e.* C(4)–C(5)–C(6)–C(11), is 98·4 (8)°. This is significantly different from the 71° found in *cyclo*-(-Gly-L-Tyr-) and the 72° found in *cyclo*(-L-Ser-L-Tyr-).

The leucyl C^{β} atom is axial to the diketopiperazine ring with N(2)–C(3)–C(12) 111 (1)°. The dihedral angle χ^1 [N(2)–C(3)–C(12)–C(13)] is −55·2 (8)°, and is much smaller than that (−72°) found in *cyclo*(-L-Pro-L-Leu-) (Karle, 1972). The leucyl side chain is in an extended conformation with χ^2, *i.e.* C(3)–C(12)–C(13)–C(14), 173·7 (7)°, as in *cyclo*-(-L-Pro-L-Leu-) ($\chi^2 = 178°$).

The diketopiperazine ring takes a boat conformation as in the case of other tyrosyl-containing diketopiperazines.

The deviations of the leucyl and tyrosyl C^{α} atoms from the mean plane passing through the remaining atoms of the diketopiperazine ring are 0·135 (7) and 0·228 (7) Å respectively.

The crystal structure is shown in Fig. 2. Adjacent molecules along **b** are connected by a pair of N–H···O hydrogen bonds. The hydrogen-bond parameters are listed in Table 2.

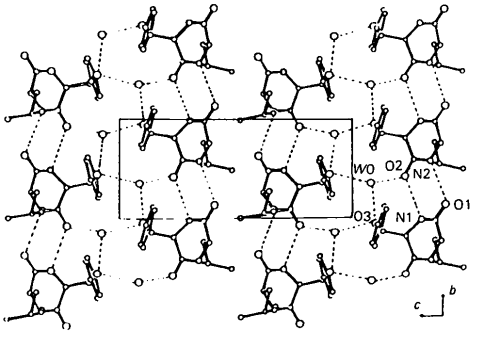
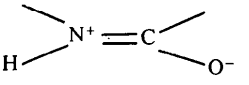


Fig. 2. Packing of the molecules viewed along **a***.

Table 2. *Hydrogen-bond parameters*

D–H···*A*	*D*···*A* (Å)	H···*A* (Å)	H–*D*···*A* (°)	Equivalent position of *A*
N(2)–H(2)···O(1)	2·894 (6)	2·02	6·6	$x, y-1, z$
N(1)–H(1)···O(2)	2·888 (9)	2·03	11·2	$x, y+1, z$
O(3)–H(3)···*WO*	2·619 (9)	1·86	11·3	$3-x, \frac{1}{2}+y, -z$
WO–H(21)···O(2)	2·734 (6)	1·94	18·3	$2-x, \frac{1}{2}+y, -z$
WO–H(22)···O(3)	2·871 (6)	1·81	8·3	x, y, z

One of the peptide O atoms [O(1)] takes part in one hydrogen bond, whereas the other one [O(2)] participates in two hydrogen bonds. This might explain the very low value of the torsion angle ω_2, since when the O atom of the peptide unit participates in the hydrogen bond, the peptide unit would be expected to have a greater contribution from the resonance structure



such that the peptide bond acquires a greater double-bond character, and the rotation angle ω would be small. In the present case, as O(2) participates in two hydrogen bonds, the rotation about N(2)–C(2) is much more restricted, and ω is small.

The C=O lengths are 1·215 (8) and 1·239 (9) Å at C(1) and C(2) respectively. The atom of the shorter bond is involved in one hydrogen bond whereas that of the longer bond is involved in two. A similar observation was made by Ramani, Venkatesan & Marsh (1978) in the structure of *cyclo*(-L-His-L-Asp-).

Another interesting feature observed in such cases is that the C′–N bond is short when C=O is long and C′–N is long when C=O is short (Venkatesan & Ramakumar, 1981). The C′–N lengths in the present structure are consistent with this observation: 1·353 (9) Å when C=O is short and 1·322 (8) Å when C=O is long.

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Structure du Complexe Tétracarbonyle(méthylènetriphénylphosphorane-*C*)fer(II), $[Fe(C_{19}H_{17}P)(CO)_4]$

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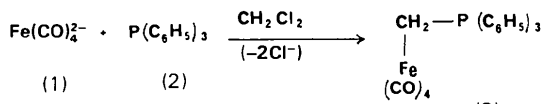
(*Reçu le 3 février* 1984, *accepté le 16 juillet* 1984)

Abstract. $M_r = 444{\cdot}2$, triclinic, $P\bar{1}$, $a = 9{\cdot}535\ (2)$, $b = 10{\cdot}824\ (2)$, $c = 11{\cdot}099\ (3)$ Å, $\alpha = 105{\cdot}40\ (3)$, $\beta = 92{\cdot}15\ (2)$, $\gamma = 108{\cdot}71\ (3)°$, $V = 1036{\cdot}4\ (4)$ Å^3, $Z = 2$, D_m (flotation in $AgNO_3$ solution) $= 1{\cdot}4$, $D_x = 1{\cdot}42$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}827$ mm^{-1}, $F(000) = 456$, room temperature, $R_w = 0{\cdot}068$ for 2960 reflexions. The methylene carbon has slightly distorted sp^3 hybridization caused by steric interactions between the phenyl and carbonyl groups. This also leads to a distortion of Fe–C–O from linear. The compound could have a betainic form.

Introduction. La réaction entre l'anion fer tétracarbonyle (1) et la triphénylphosphine (2) en présence de dichlorométhane conduit à la formation du composé (3):



La structure ylure complexé ci-dessus a été proposée à la suite d'un ensemble d'études spectroscopiques (RMN ^{1}H, ^{13}C, ^{31}P, spectrométrie de masse *etc.*). Cependant la nature originale de cette structure et les controverses soulevées ont rendu nécessaire la confirmation par une étude à l'aide de rayons X.

Partie expérimentale. Cristaux (polyèdres jaunes de diamètre 0,25 mm) cristallisés à basse température (255 K) à l'abri de l'oxygène à partir d'une solution CH_2Cl_2/hexane; mesures effectuées à l'abri de l'air sur diffractomètre CAD-4 Enraf–Nonius du Centre de Diffractométrie de l'Université de Rennes, monochromateur graphite, balayage $\omega/2\theta = 1$, temps maximum: 60 s, $\theta_{max} = 30°$, réflexions de contrôle: $\bar{1}\bar{2}2$, $\bar{2}\bar{1}3$, 003 (± 1,2%), secteur analysé HKL: $\bar{1}3,13,\bar{1}5$, 15,0,15. L'enregistrement a fourni 6327 mesures dont 6037 plans uniques [2960 avec $I > 3\sigma(I)$] avec $R_{int} = 0{,}022$. Paramètres de la maille affinés avec 25 réflexions. Structure résolue à l'aide d'une fonction de Patterson: après élimination des pics dus aux vecteurs Fe–P et P–P, pic n° 3 choisi pour calculer les coordonnées de Fe. Affinements et différences de Fourier effectués avec les réflexions les plus intenses ne donnant aucun résultat, un jeu de 600 réflexions d'intensité moyenne a été déterminé en prenant: $2\sigma(I) < I < 5\sigma(I)$ et $0{,}15 < \sin\theta/\lambda < 0{,}40$ Å^{-1}. Ce jeu donnant $R = 0{,}53$ a été conservé dans les nombreux affinements et différences de Fourier nécessaires pour trouver les atomes restant. Après affinement isotrope ($R = 0{,}104$) puis anisotrope ($R = 0{,}082$) des atomes non hydrogène, dernière différence de Fourier révèle des atomes d'hydrogène (entre 0,72 et 0,34 e Å^{-3}). Dernier affinement, basé sur F^2, sur tous les paramètres (sauf les coefficients d'agitation thermiques des atomes d'hydro-

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