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Acta Cryst. (1993). C**49**, 1673–1676

Structure of a 1:1 Complex Between L-Asp-L-Phe and L-His-Gly

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(*Received* 13 *March* 1992; *accepted* 8 *March* 1993)

Abstract

Both molecules occur in slightly folded conformations, characterized by $\varphi_2 = -93.7°$ in L-His-Gly and an unusual $\varphi_2 = 60.2°$ in L-Asp-L-Phe. The peptide linkage of L-His-Gly displays a substantial deviation from planarity with $\omega_1 = -163.5°$. The crystal packing is arranged in thick hydrophilic layers separated by hydrophobic sheets composed of L-Phe aromatic side chains. There are numerous hydrogen bonds, including an extremely short contact [O···N = 2.532 (6) Å] between the ionized L-Asp and L-His side chains.

Comment

The problems of preparing peptide crystals suitable for diffraction purposes are familiar to most researchers working in the field. One solution to such difficulties is to utilize more sophisticated crystallization techniques (see, for example, Eggleston & Baures, 1992) than slow evaporation, the method most frequently used. Another alternative is to take advantage of the acidic and basic properties of peptides by crystallizing them as salts, usually as cations in *e.g.* hydrochlorides. When investigations are performed with regard to the biological activities exhibited by these molecules, the potentially most interesting ionization state is that observed in aqueous solution at physiological pH. In connection with this, the number of acidic residues in the peptide, n_A, and the number of basic residues, n_B, are of importance. When $n_A = n_B = 0$, or generally when $n_A = n_B$, peptide cations always possess protonated C-terminal carboxylate groups. Since associated pK_a values normally range from 1.7 to 2.6, this corresponds to unphysiologically low pH values. If, however, the peptide in question has $n_A > n_B$ or $n_B > n_A$ it can be crystallized as an anion or a cation in a salt while retaining its physiological protonation state. It is surprising that only a single example is known where this technique has been employed, namely in the structure of L-Pro-L-Lys acetate (Urpi, Coll, Subirana, Solans & Font-Alba, 1988). This means that for acidic and basic peptides there is a large unexplored potential for finding suitable counterions that could facilitate crystal growth. A special option, based on extensive studies of 1:1 amino acid–amino acid salts (Soman, Vijayan, Ramakrishnan & Row, 1990, and references therein), is to cocrystallize two different peptides with opposite charges, as in the L-His-L-Ser Gly-L-Glu 1:1 complex (Suresh & Vijayan, 1985). In the work presented here, we have used this latter approach to study the 1:1 cocrystalline complex between the dipeptides L-Asp-L-Phe and L-His-Gly. Neither of the two individual compounds has been subject to investigation by X-ray diffraction in the past. In addition to providing suitable crystals for X-ray analysis of molecular structure, cocrystallization also presents interesting opportunities to study intermolecular interactions between different molecules in the solid phase.

The asymmetric unit, which consists of one L-Asp-L-Phe anion, one L-His-Gly cation and a solvent water molecule, is depicted in Fig. 1. Molecular geometry is given in Table 2. There are no remarkable values, although the C3*A*—C4*A* bond length (1.564 Å) is clearly in the upper range of what is normally encountered for this kind of C—C single bond [average 1.520 Å (Allen *et al.*, 1987)].

The side chains of L-Asp-L-Phe have normal *gauche*$^-$ orientations, but the main chain exhibits a very unusual folded conformation that places both the side chains on the same side of the peptide plane, the result of an ordinary ψ_1 value (154.5°) combined with a unique positive φ_2 value (60.2°). Only once has a similar arrangement been observed in the structure of an L-L dipeptide, namely for L-Tyr-L-Lys (Urpi, Coll & Subirana, 1988) with $\psi_1 = 111.3$ and $\varphi_2 = 52.7°$. The L-His-Gly main-chain conformation is folded in a usual manner with $\varphi_2 = -93.7°$. The peptide bond unit of this molecule is remarkably

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twisted with $\omega_1 = -163.5°$. Peptide-bond distortions $>15°$ are very rare; a search of the Cambridge Structural Database (1984) revealed only nine occurrences in structures of linear peptides. The extreme value, 156.6°, was observed for *N*-(*tert*-butoxycarbonyl)prolyl-leucine benzyl ester (Sugino, Tanaka & Ashida, 1978). Usually, these distortions are accompanied by fairly short intermolecular hydrogen bonds involving the peptide carbonyl group (Feldman & Eggleston, 1990), but this is not the situation in the structure presented here. Apparently, instead, C3*B* is pushed out of the peptide plane to optimize the hydrogen-bonding arrangement of the Gly carboxylate group. The L-His side chain is *gauche*$^+$ while $\chi_1^2 = -93.6°$. This $\chi_{His}^1 - \chi_{His}^2$ combination is commonly observed for His residues in small peptides.

While the unlike molecules in the crystal structure of 1:1 L-His-L-Ser Gly-L-Glu (Suresh & Vijayan, 1985) segregate into separate alternating layers, molecular packing in the present crystal structure is governed by the aggregation of hydrophilic and hydrophobic groups. It can be seen from Fig. 2 that the aromatic side chains of the L-Phe residues form hydrophobic sheets separating thick hydrophilic layers encompassing the remainder of the Asp-Phe molecules and the His-Gly molecules. An inspection of intermolecular distances reveals that there are no favourable aromatic interactions between phenyl rings related by the twofold screw axis along *b* (Fig. 2). Instead, rings related by translation along the short *a* axis (interplanar angle = 0°) stack in a parallel-plate configuration (Gould, Gray, Taylor & Walkinshaw, 1985) without the edge-to-face interactions typical for the 'herringbone' packing patterns (interplanar angles between 40 and 85°) frequently observed for phenyl groups in peptide crystals. However, edge-to-phase interactions do occur, but they involve Phe-ring–His-imidazole-ring contacts (Fig. 2). The relevant intermolecular distances are C10*A*···H8*B* (2.95 Å) and C11*A*···H8*B* (2.99 Å). There is also an oxygen–aromatic interaction with (C10*A*—)H10*A*···O5*A* = 2.53 Å. O5*A* is close to the optimal ring-edge position, estimated to be worth around 8 kJ mol^{-1} (Thomas, Smith, Thomas & Feldmann, 1982).

The numerous hydrogen bonds in the crystal structure are listed in Table 3. Counting a carboxylate group as a fourfold acceptor, the water molecule as a twofold acceptor and the peptide carbonyl as a single acceptor, there is a total of 16 acceptors in the asymmetric unit, but only 12 O—H and N—H donors. Thus, it is obvious that all the acceptors cannot utilize their full hydrogen-bonding potential. As is often observed in such cases, peptide carbonyl groups lose in the competition for active H atoms, but instead participate in C^{α}—H···O=C< interactions. The two distances (C1*A*—)H1*A*···O1*A* = 2.23 Å and (C1*B*—)H1*B*···O1*B* = 2.13 Å are comparatively very short for such contacts (Taylor & Kennard, 1982). The solvent water molecule donates two, but accepts only one hydrogen bond, the most commonly observed hydrogen-bond pattern for water molecules in peptide structures (Görbitz & Etter, 1992). Curiously enough, the remaining 11 O—H and N—H protons do not form an even distribution between the three carboxylate groups in the structure. The C-terminal carboxylate group of L-His-Gly participates in two interactions with water molecules, one with each of the two different N-terminal amino groups, as well as a weak contact with a peptide >N—H, giving a total of five accepted H atoms. The C-terminal carboxylate of L-Asp-L-Phe accepts four H atoms, including one donated by the His side chain. This means that the Asp side-chain carboxylate is very unusual in accepting only two H atoms (not counting the C^{phenyl}—H···O interaction described above) (Görbitz & Etter, 1992). However, one of these interactions is an extremely short N—H···O contact with the N^{τ}—H of the His side chain. The N4*B*···O5*A* dis-

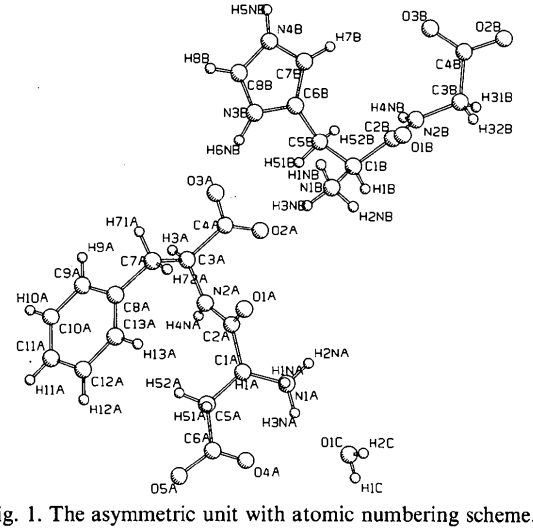

Fig. 1. The asymmetric unit with atomic numbering scheme.

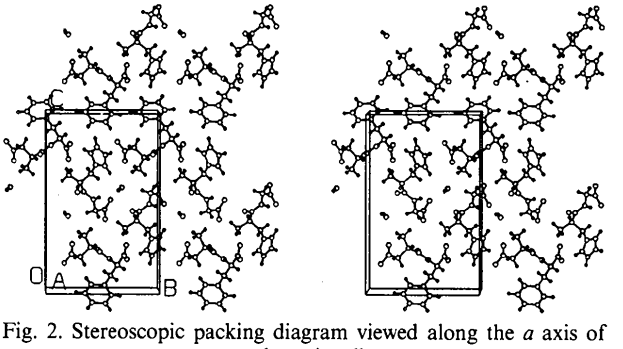

Fig. 2. Stereoscopic packing diagram viewed along the *a* axis of the unit cell.

tance is 2.532 (6) Å, presumably making it the shortest such hydrogen bond ever observed (Görbitz, 1989). Since O5*A* accepts no other H atoms, it is a very potent acceptor, and the favourable geometry of the interaction may also contribute to this unprecedented short N···O distance. Bond lengths and bond angles for heavy atoms in the imidazole ring vary depending on the presence of a proton on N^{π}. For instance, N^{τ}—C^{2} and C^{2}—N^{τ}—C^{4} average 1.318 Å and 109.3° in $HisH^{+}$, but 1.342 Å and 105.3° in His (neutral) (Görbitz, 1989). Thus, although all imidazole H atoms were introduced in theoretical positions, the values observed for N4*B*—C8*B* [1.320 (7) Å] and C6*B*—N3*B*—C8*B* [108.6 (4)°] together with remaining ring geometry, unequivocally confirm the protonated state of the His side chain. Nevertheless, the molecular geometry of the accepting carboxylate group is clearly affected by the strong hydrogen bond. C6*A*—O5*A* is elongated to 1.276 (7) Å, while C6*A*—O4*A* measures only 1.229 (6) Å. The associated bond angles are C5*A*—C6*A*—O5*A* = 112.7 (5) and C5*A*—C6*A*—O4*A* = 121.2 (5)° (Table 2), values which are commonly observed for protonated carboxyl groups.

One of the postulated hydrogen-bond rules (Etter, 1990) for hydrogen-bond patterns in crystal structures, states that the best donor should form a hydrogen bond with the best acceptor. Since in the present structure these are represented by the imidazole group and the Asp carboxylate group, respectively, the occurrence of the strong side-chain–side-chain interaction is not unexpected. In the L-His-L-Ser Gly-L-Glu cocrystal (Suresh & Vijayan, 1985), there is also a very short side-chain–side-chain interaction with N^{τ}—H···O = 2.620 (7) Å. However, no such contacts occur in the crystal structures of the related complexes L-His L-Asp (Bhat & Vijayan, 1978) and L-His L-Asp monohydrate (Suresh & Vijayan, 1987).

Experimental

Crystal data

$C_8H_{13}N_4O_3^+.C_{13}H_{15}N_2O_5^-.H_2O$	D_x = 1.485 Mg m^{-3}
M_r = 510.50	Mo $K\alpha$ radiation
Monoclinic	λ = 0.71069 Å
$P2_1$	Cell parameters from 25 reflections
a = 5.052 (4) Å	θ = 10.2–16.3°
b = 11.950 (9) Å	μ = 0.11 mm^{-1}
c = 18.985 (7) Å	T = 172 K
β = 94.88 (5)°	Plates
V = 1142 (2) Å^3	0.550 × 0.30 × 0.150 mm
Z = 2	Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer	R_{int} = 0.057
ω-2θ scans	θ_{max} = 24.0°
Absorption correction: none	$h = 0 \rightarrow 5$
4030 measured reflections	$k = -13 \rightarrow 13$
1888 independent reflections	$l = -21 \rightarrow 21$
1558 observed reflections [$I > 2\sigma(I)$]	3 standard reflections intensity variation: 7.2%

Refinement

Refinement on F^2	$w = 4F_o^2/\sigma^2(F_o)^2$
Final R = 0.046	$(\Delta/\sigma)_{max}$ = 0.01
wR = 0.051	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
S = 1.14	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
1558 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
222 parameters	
H-atom parameters not refined except those of amino groups and water	

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

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

	x	y	z	B_{eq}
O1*A*	0.8637 (7)	0.4535	0.2417 (2)	2.2 (2)
O2*A*	0.9080 (8)	0.7066 (5)	0.2694 (2)	2.1 (2)
O3*A*	0.6086 (7)	0.7168 (4)	0.1783 (2)	2.0 (2)
O4*A*	1.6995 (7)	0.2222 (4)	0.2981 (2)	1.7 (1)
O5*A*	1.653 (1)	0.1532 (5)	0.1884 (2)	2.9 (2)
N1*A*	1.199 (1)	0.3341 (5)	0.3307 (2)	1.43 (8)
N2*A*	1.1949 (8)	0.5514 (5)	0.1987 (2)	1.31 (8)
C1*A*	1.307 (1)	0.3850 (6)	0.2677 (3)	1.3 (1)
C2*A*	1.101 (1)	0.4678 (6)	0.2362 (3)	1.3 (1)
C3*A*	1.014 (1)	0.6266 (5)	0.1579 (3)	1.6 (1)
C4*A*	0.829 (1)	0.6888 (5)	0.2071 (3)	1.4 (1)
C5*A*	1.363 (1)	0.2965 (6)	0.2141 (3)	1.7 (1)
C6*A*	1.593 (1)	0.2192 (6)	0.2375 (3)	1.8 (1)
C7*A*	0.859 (1)	0.5686 (6)	0.0955 (3)	1.7 (1)
C8*A*	1.041 (1)	0.5099 (6)	0.0485 (3)	1.7 (1)
C9*A*	1.183 (1)	0.5682 (6)	0.0009 (3)	2.1 (1)
C10*A*	1.359 (1)	0.5134 (6)	−0.0394 (3)	2.6 (1)
C11*A*	1.391 (1)	0.3994 (7)	−0.0330 (3)	2.9 (1)
C12*A*	1.251 (1)	0.3399 (6)	0.0134 (3)	2.7 (1)
C13*A*	1.071 (1)	0.3953 (6)	0.0531 (3)	2.0 (1)
O1*B*	0.0608 (8)	0.7759 (4)	0.4349 (2)	2.2 (2)
O2*B*	−0.2382 (8)	1.0125 (4)	0.5785 (2)	2.0 (2)
O3*B*	−0.1274 (8)	1.0630 (5)	0.4722 (2)	2.4 (2)
N1*B*	0.406 (1)	0.7042 (5)	0.3489 (3)	1.63 (8)
N2*B*	0.311 (1)	0.9184 (5)	0.4820 (2)	1.94 (9)
N3*B*	0.3392 (9)	0.8949 (5)	0.2228 (2)	1.53 (8)
N4*B*	0.025 (1)	1.0180 (5)	0.2254 (2)	1.77 (8)
C1*B*	0.486 (1)	0.8054 (5)	0.3916 (3)	1.5 (1)
C2*B*	0.264 (1)	0.8321 (6)	0.4380 (3)	1.5 (1)
C3*B*	0.151 (1)	0.9335 (6)	0.5407 (3)	2.4 (1)
C4*B*	−0.089 (1)	1.0105 (6)	0.5283 (3)	1.6 (1)
C5*B*	0.568 (1)	0.9000 (6)	0.3445 (3)	1.6 (1)
C6*B*	0.357 (1)	0.9381 (5)	0.2900 (3)	1.4 (1)
C7*B*	0.161 (1)	1.0147 (6)	0.2910 (3)	1.6 (1)
C8*B*	0.136 (1)	0.9451 (6)	0.1849 (3)	1.8 (1)
O1*C*	1.379 (1)	0.1896 (5)	0.4424 (2)	2.6 (2)

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

O1*A*—C2*A*	1.222 (6)	O3*B*—C4*B*	1.237 (6)
O2*A*—C4*A*	1.233 (6)	N1*B*—C1*B*	1.492 (7)
O3*A*—C4*A*	1.246 (6)	N2*B*—C2*B*	1.337 (7)
O4*A*—C6*A*	1.229 (6)	N2*B*—C3*B*	1.442 (7)
O5*A*—C6*A*	1.276 (7)	N3*B*—C6*B*	1.373 (6)
N1*A*—C1*A*	1.486 (7)	N3*B*—C8*B*	1.341 (7)

N2*A*—C2*A*	1.337 (7)	N4*B*—C7*B*	1.370 (7)
N2*A*—C3*A*	1.457 (7)	N4*B*—C8*B*	1.320 (7)
C1*A*—C2*A*	1.523 (7)	C1*B*—C2*B*	1.518 (8)
C1*A*—C5*A*	1.511 (7)	C1*B*—C5*B*	1.520 (7)
C3*A*—C4*A*	1.564 (7)	C3*B*—C4*B*	1.525 (8)
C3*A*—C7*A*	1.530 (8)	C5*B*—C6*B*	1.490 (7)
C5*A*—C6*A*	1.521 (8)	C6*B*—C7*B*	1.353 (7)
C7*A*—C8*A*	1.507 (8)	O1*C*—H1*C*	0.9 (1)
O1*B*—C2*B*	1.224 (7)	O1*C*—H2*C*	0.80 (9)
O2*B*—C4*B*	1.266 (6)		
C2*A*—N2*A*—C3*A*	120.6 (4)	C6*B*—N3*B*—C8*B*	108.6 (4)
N1*A*—C1*A*—C2*A*	107.2 (4)	C7*B*—N4*B*—C8*B*	107.8 (5)
N1*A*—C1*A*—C5*A*	110.9 (5)	N1*B*—C1*B*—C2*B*	107.8 (4)
C2*A*—C1*A*—C5*A*	110.5 (4)	N1*B*—C1*B*—C5*B*	110.9 (4)
O1*A*—C2*A*—N2*A*	123.0 (5)	C2*B*—C1*B*—C5*B*	115.6 (5)
O1*A*—C2*A*—C1*A*	121.3 (5)	O1*B*—C2*B*—N2*B*	123.8 (5)
N2*A*—C2*A*—C1*A*	115.6 (4)	O1*B*—C2*B*—C1*B*	121.1 (5)
N2*A*—C3*A*—C4*A*	110.7 (4)	N2*B*—C2*B*—C1*B*	115.1 (5)
N2*A*—C3*A*—C7*A*	112.9 (4)	N2*B*—C3*B*—C4*B*	116.4 (5)
C4*A*—C3*A*—C7*A*	112.7 (4)	O2*B*—C4*B*—O3*B*	125.3 (5)
O2*A*—C4*A*—O3*A*	125.4 (5)	O2*B*—C4*B*—C3*B*	114.3 (5)
O2*A*—C4*A*—C3*A*	119.7 (5)	O3*B*—C4*B*—C3*B*	120.3 (5)
O3*A*—C4*A*—C3*A*	115.0 (4)	C1*B*—C5*B*—C6*B*	115.0 (5)
C1*A*—C5*A*—C6*A*	114.2 (4)	N3*B*—C6*B*—C5*B*	121.2 (5)
O4*A*—C6*A*—O5*A*	126.1 (5)	N3*B*—C6*B*—C7*B*	106.0 (4)
O4*A*—C6*A*—C5*A*	121.2 (5)	C5*B*—C6*B*—C7*B*	132.7 (5)
O5*A*—C6*A*—C5*A*	112.7 (5)	N4*B*—C7*B*—C6*B*	108.5 (5)
C3*A*—C7*A*—C8*A*	111.9 (4)	N3*B*—C8*B*—N4*B*	109.1 (5)
C2*B*—N2*B*—C3*B*	120.0 (5)	H1*C*—O1*C*—H2*C*	117 (8)

ψ_1	(N1*A*—C1*A*—C2*A*—N2*A*)	154.5 (4)
ω_1	(C1*A*—C2*A*—N2*A*—C3*A*)	171.4 (4)
φ_2	(C2*A*—N2*A*—C3*A*—C4*A*)	60.2 (6)
ψ_T	(N2*A*—C3*A*—C4*A*—O2*A*)	28.3 (7)
χ_1^1	(N1*A*—C1*A*—C5*A*—C6*A*)	−68.9 (6)
χ_1^2	(C1*A*—C5*A*—C6*A*—O4*A*)	8.0 (8)
χ_2^1	(N2*A*—C3*A*—C7*A*—C8*A*)	−54.1 (6)
χ_2^2	(C3*A*—C7*A*—C8*A*—C9*A*)	−76.8 (7)
ψ_1	(N1*B*—C1*B*—C2*B*—N2*B*)	177.2 (5)
ω_1	(C1*B*—C2*B*—N2*B*—C3*B*)	−163.5 (5)
φ_2	(C2*B*—N2*B*—C3*B*—C4*B*)	−93.7 (6)
ψ_T	(N2*B*—C3*B*—C4*B*—O2*B*)	173.1 (5)
χ_1^1	(N1*B*—C1*B*—C5*B*—C6*B*)	59.9 (6)
χ_1^2	(C1*B*—C5*B*—C6*B*—N3*B*)	−93.6 (6)

Table 3. *Hydrogen-bond and close-contact distances* (Å) *and angles* (°)

D—H···O	*D*—H	H···O	*D*···O	*D*—H···O
N1*A*—H1N*A*···O4*A*^{i}	0.97 (6)	1.91 (6)	2.887 (7)	174 (5)
N1*A*—H2N*A*···O2*B*^{ii}	0.88 (5)	1.88 (6)	2.739 (6)	164 (5)
N1*A*—H3N*A*···O1*C*	0.92 (6)	2.03 (6)	2.823 (7)	144 (5)
N2*A*—H4N*A*···O3*A*^{iii}	0.95	2.23	2.926 (6)	129
C1*A*—H1*A*···O1*A*^{iii}	0.95	2.23	3.009 (6)	138
N1*B*—H1N*B*···O2*A*^{i}	0.88 (6)	1.97 (6)	2.824 (7)	161 (5)
N1*B*—H2N*B*···O2*B*^{iv}	0.93 (8)	1.95 (8)	2.840 (6)	161 (6)
N1*B*—H3N*B*···O2*A*	1.01 (5)	2.08 (5)	3.059 (7)	164 (4)
N2*B*—H4N*B*···O2*B*^{iii}	0.95	2.47	3.016 (6)	117
N2*B*—H4N*B*···O3*B*^{iii}	0.95	2.41	3.341 (7)	165
N3*B*—H6N*B*···O3*A*	0.95	1.77	2.701 (6)	168
N4*B*—H5N*B*···O5*A*^{v}	0.95	1.59	2.532 (6)	173
C1*B*—H1*B*···O1*B*^{iii}	0.95	2.13	2.970 (7)	146
O1*C*—H1*C*···O3*B*^{vi}	0.9 (1)	2.1 (1)	2.932 (7)	161 (7)
O1*C*—H2*C*···O3*B*^{vii}	0.80 (9)	2.27 (9)	3.064 (7)	170 (8)

Symmetry code: (i) $x-1, y, z$; (ii) $1-x, y-0.5, 1-z$; (iii) $x+1, y, z$; (iv) $-x, y-0.5, -z$; (v) $x-2, y+1, z$; (vi) $x+2, y-1, z$; (vii) $x-1, y-1, z$.

Small clusters of crystals were grown by vapour diffusion of 2-propanol into an aqueous solution containing equimolar amounts of L-Asp-L-Phe and L-His-Gly. The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens *et al.*, 1984). Unrefined H atoms were introduced in theoretical positions with d_{X-H} = 0.95 Å and fixed isotropic $B = 1.2 \times B$ of the bonded atom. Only O atoms were refined anisotropically in the final cycle of full-matrix least-squares refinement. All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985).

The authors thank Professor Doyle Britton, Department of Chemistry, University of Minnesota, for solving the crystal structure. Helpful discussions with John MacDonald, University of Minnesota, are appreciated. This work was supported by an NIH grant (GM 42148-01) to MCE.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71141 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR1004]

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