The conformation of dehydro-Phe-Ala-OH corresponds to the minimum-energy region V in the conformational energy map of the dehydro-Phe residue (Ajò, Casarin & Granozzi, 1982; Ajò, Busetti & Granozzi, 1982; see in particular Fig. 6 in the latter) while that of the corresponding fragment in (dehydro-Phe)$_2$-Ala-OH is related to region II. This difference can be ascribed to the different intermolecular packing; the intramolecular ten-membered ring suggested for doubly unsaturated *N*-acetyltripeptides (Pieroni, Fissi, Merlino & Ciardelli, 1976–77) is obviously impossible for the dipeptide dehydro-Phe-Ala-OH but is also absent in the crystal structure of (dehydro-Phe)$_2$-Ala-OH.

The conformation of the alanine residue is described by the following values of the torsion angles:

ω_2[C(3)—C(4)—N(2)—C(12)] = 180 (1),
φ_2[C(4)—N(2)—C(12)—C(14)] = −75 (1),
ψ_2[N(2)—C(12)—C(14)—O(2)] = 160 (1)°.

This conformation of the alanine residue was described as the preferred one (Nakayama, Maeda, Kaneko & Katsura, 1971) for dehydrophenylalanyl dipeptides in relation to their asymmetric reduction. However, it is different from that of the same residue in (dehydro-Phe)$_2$-Ala.

These results point to a relevant mutual influence between the conformation of unsaturated residues and the nature and conformation of the following saturated one. This further supports our idea that conformational flexibility of unsaturated residues is similar to that of the saturated ones. In fact, previously reported theoretical predictions on this class of compounds is now further corroborated, since experimental conformations correspond to low calculated energy regions, and several predicted minimum-energy regions are populated.

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Structure of L-Tyrosyl-L-valine Monohydrate, $C_{14}H_{20}N_2O_4.H_2O$

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Abstract. $M_r = 298{\cdot}34$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}629$ (1), $b = 8{\cdot}702$ (2), $c = 31{\cdot}007$ (8) Å, $V = 1519$ (1) Å^3, $Z = 4$, $D_m = 1{\cdot}31$, $D_x = 1{\cdot}30$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}737$ mm^{-1}, $F(000) = 640{\cdot}0$, $T = 293$ K, final $R = 0{\cdot}071$ for 1144 unique observed reflections. The crystal structure is stabilized by extensive hydrogen-bonding involving N and O atoms. The molecule exists as a zwitterion with the

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N-terminal end protonated. The side-chain conformations are as expected with χ^{11}, χ^{12}, χ^{22}, χ^{21} 174 (1), −60 (1), −101 (1) and 81 (1)°, respectively.

Introduction. We report here the structure of the title compound as part of our investigation on peptides which are possibly involved in specific interaction with nucleic acids.

Experimental. Dipeptide purchased from Sigma used without purification; needle-like crystals by evaporation from aqueous solution; $\theta_{max} = 60°$, CAD-4 diffractometer; crystal 0·16 × 0·1 × 1·2 mm; 1352 reflections measured; 1144 considered observed [$F_o \geq 3\sigma(F_o)$]; 2 strong reflections monitored periodically during data collection showed little variation; unit-cell parameters refined using 25 high-angle reflections; Lorentz and polarization corrections applied, no absorption correction; index range h 0 to 6, k 0 to 10, l 0 to 34; D_m by flotation in acetone/bromoform; structure solved by direct methods using *MULTAN* (Main, Woolfson & Germain, 1971). Block-diagonal least-squares refinement (Shiono, 1965); $\sum w(|F_o| - |F_c|)^2$ minimized; water and N(1) H atoms located from difference Fourier map, remaining H's geometrically fixed; refinement (non-H anisotropic, H isotropic) converged at $R = 0{\cdot}071$, $R_w = 0{\cdot}097$, $w = 1/\sigma^2(F_o)$; $(\Delta/\sigma)_{max} = 0{\cdot}38$, $\Delta\rho = \pm 0{\cdot}4$ e Å^{-3}. The scattering factors for H atoms obtained from Stewart, Davidson & Simpson (1965) and for heavy atoms computed from the function of Cromer & Waber (1965).

Discussion. The molecular structure and atomic numbering are shown in Fig. 1, and final positional parameters are listed in Table 1.* Bond lengths, bond angles and conformation angles (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) are listed in Table 2.

* Lists of structure amplitudes, anisotropic thermal parameters, H atom coordinates, bond lengths and angles involving H and hydrogen-bond parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39331 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

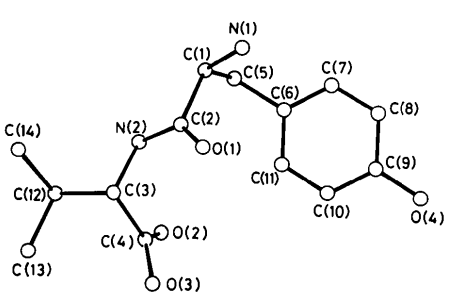

Fig. 1. Molecular structure and atomic numbering.

Table 1. *Final positional parameters* (×10⁴) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}(Å²)
O(1)	−813 (9)	8239 (6)	3766 (2)	3·40 (14)
O(2)	2622 (8)	4697 (6)	4029 (2)	3·84 (14)
O(3)	−745 (10)	3700 (6)	3786 (2)	3·73 (15)
O(4)	368 (10)	6637 (6)	1801 (2)	3·93 (14)
*W*O(1)	−4789 (10)	2072 (6)	3958 (2)	4·38 (15)
N(1)	−4450 (12)	9672 (6)	3433 (2)	3·06 (16)
N(2)	−2974 (9)	6378 (6)	4097 (2)	2·29 (13)
C(1)	−4994 (11)	8129 (8)	3604 (2)	2·35 (17)
C(2)	−2677 (12)	7580 (8)	3833 (2)	2·27 (17)
C(3)	−993 (13)	5688 (7)	4314 (2)	2·17 (17)
C(4)	390 (12)	4619 (8)	4016 (2)	2·71 (18)
C(5)	−5804 (13)	7042 (8)	3246 (2)	2·73 (18)
C(6)	−4119 (12)	6963 (7)	2865 (2)	2·11 (16)
C(7)	−2097 (13)	6046 (8)	2874 (2)	2·69 (21)
C(8)	−603 (15)	5941 (9)	2521 (2)	2·91 (18)
C(9)	−1119 (13)	6750 (8)	2148 (2)	2·75 (18)
C(10)	−3123 (15)	7679 (9)	2126 (2)	2·99 (19)
C(11)	−4603 (15)	7760 (9)	2492 (2)	3·06 (20)
C(12)	−1848 (13)	4791 (9)	4718 (2)	2·82 (19)
C(13)	189 (17)	3928 (11)	4923 (3)	5·67 (28)
C(14)	−3112 (20)	5826 (11)	5037 (3)	5·22 (29)

Table 2. *Bond distances* (Å), *angles and conformation angles* (°) *with e.s.d.'s in parentheses*

N(1)–C(1)	1·476 (9)	C(5)–C(6)	1·516 (10)
C(1)–C(2)	1·560 (9)	C(6)–C(7)	1·391 (10)
C(1)–C(5)	1·529 (10)	C(6)–C(11)	1·376 (10)
C(2)–O(1)	1·214 (8)	C(7)–C(8)	1·382 (11)
C(2)–N(2)	1·339 (9)	C(8)–C(9)	1·387 (11)
N(2)–C(3)	1·434 (9)	C(9)–C(10)	1·389 (11)
C(3)–C(4)	1·524 (10)	C(9)–O(4)	1·366 (9)
C(3)–C(12)	1·554 (10)	C(10)–C(11)	1·410 (11)
C(4)–O(2)	1·259 (8)	C(12)–C(13)	1·510 (12)
C(4)–O(3)	1·247 (9)	C(12)–C(14)	1·513 (12)
C(2)–N(2)–C(3)	121·1 (6)	C(5)–C(6)–C(7)	121·6 (6)
N(1)–C(1)–C(2)	105·6 (5)	C(5)–C(6)–C(11)	120·5 (6)
N(1)–C(1)–C(5)	111·3 (6)	C(7)–C(6)–C(11)	117·9 (6)
C(2)–C(1)–C(5)	113·0 (6)	C(6)–C(7)–C(8)	121·4 (7)
O(1)–C(2)–N(2)	125·6 (6)	C(7)–C(8)–C(9)	120·0 (7)
O(1)–C(2)–C(1)	120·0 (6)	O(4)–C(9)–C(8)	119·5 (7)
N(2)–C(2)–C(1)	114·4 (6)	O(4)–C(9)–C(10)	120·0 (7)
N(2)–C(3)–C(4)	111·7 (6)	C(8)–C(9)–C(10)	120·4 (7)
N(2)–C(3)–C(12)	110·4 (6)	C(9)–C(10)–C(11)	118·0 (7)
C(4)–C(3)–C(12)	109·9 (6)	C(6)–C(11)–C(10)	122·4 (7)
O(2)–C(4)–O(3)	124·3 (7)	C(3)–C(12)–C(13)	110·7 (6)
O(2)–C(4)–C(3)	117·3 (6)	C(3)–C(12)–C(14)	111·9 (6)
O(3)–C(4)–C(3)	118·4 (6)	C(13)–C(12)–C(14)	112·3 (7)
C(1)–C(5)–C(6)	114·0 (6)		

N(1)–C(1)–C(2)–N(2)	ψ_1	164·5 (6)
C(2)–N(2)–C(3)–C(4)	φ_2	−79·3 (8)
C(1)–C(2)–N(2)–C(3)	ω	176·8 (8)
N(1)–C(1)–C(5)–C(6)	χ^1	52·6 (7)
C(1)–C(5)–C(6)–C(11)	χ^{22}	−101·1 (8)
C(1)–C(5)–C(6)–C(7)	χ^{21}	81·4 (8)
N(2)–C(3)–C(12)–C(13)	χ^{11}	174·2 (6)
N(2)–C(3)–C(12)–C(14)	χ^{12}	−59·7 (8)

The molecule exists as a zwitterion with the N-terminal end protonated. The side-chain conformation of tyrosine, χ^{21}, χ^{22} (Table 2), is very similar to that in L-tyrosyl-L-glutamic acid monohydrate (Pandit, Seshadri & Viswamitra, 1984). The side-chain conformation of valine, χ^{12}, χ^{11} (Table 2), shows very good

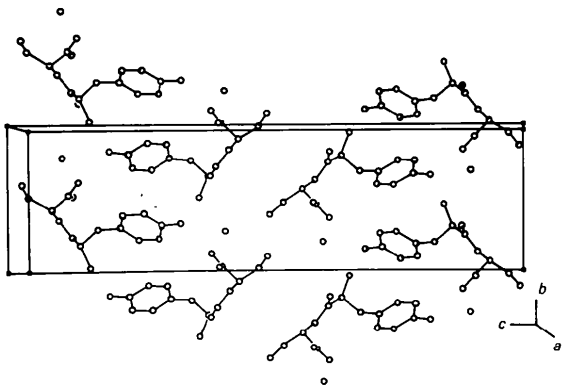

Fig. 2. View of crystal packing along **a**.

agreement with classical energy calculations (Ponnuswamy & Sasisekharan, 1971). As can be seen from Fig. 2, the tyrosine ring does not stack in the crystal lattice. The water molecule forms hydrogen bonds with the amino and carboxyl terminals of the dipeptide molecules (Fig. 2).

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Conformation and Structure of L-Valyl-L-glutamic Acid, $C_{10}H_{18}N_2O_5$

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Abstract. $M_r = 246{\cdot}3$, orthorhombic, $P2_12_12$, $a = 16{\cdot}781\ (7)$, $b = 13{\cdot}827\ (4)$, $c = 5{\cdot}367\ (4)$ Å, $V = 1245{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}313$, $D_m = 1{\cdot}30\ (2)$ Mg m^{-3}, Mo $K\alpha$ radiation ($\lambda K\alpha_1 = 0{\cdot}70926$, $\lambda K\alpha_2 = 0{\cdot}71354$ Å), $\mu = 0{\cdot}099$ mm^{-1}, $F(000) = 528$, $T = 293$ K. Final $R = 0{\cdot}038$ for 1374 observations. The dipeptide crystallizes as a zwitterion with the main-chain carboxyl ionized and the amino terminus protonated. The configuration of the peptide bond is *trans* with an ω torsion angle of 175°. The peptide backbone is in an extended conformation as is the glutamyl side chain. There is extensive intermolecular hydrogen bonding in the crystal lattice.

Introduction. Acidic amino-acid residues are of primary importance in the binding of calcium and magnesium in proteins (Kretsinger & Nelson, 1976). In addition, the role of acidic amino acids in the molecular basis for the sweet taste has been well documented (Ariyoshi, 1976; Lelj, Tancredi, Temussi & Toniolo, 1976; Goodman & Gilon, 1975; Chorev, Willson & Goodman, 1977; Murai, Ajisaka, Nobuya, Takeuchi, Kamisaku & Masagaki, 1975). Thus, the conformational and structural properties of peptides containing acidic residues are of considerable interest.

Examination of the primary sequences of many known calcium-binding proteins reveals a virtual absence of valine preceding an acidic residue in regions known or proposed to be involved in calcium binding. The possible conformational influence(s) of the hydrophobic β-branched valine residue on an adjacent glutamic acid residue thus prompted the extension of our structural studies on the conformational properties of peptides containing acidic residues (Eggleston, Valente & Hodgson, 1981*a*,*b*; Eggleston & Hodgson, 1982*a*,*b*,*c*; Eggleston & Hodgson, 1983*a*,*b*) to examine the L-valyl-L-glutamic acid molecule.

Experimental. White powder from Vega Biochemicals, Inc., colorless rods grown by slow evaporation of an aqueous methanol solution, crystal 0·4 × 0·4 × 0·5 mm, D_m measured by flotation in methylene

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