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Structure of an Antigelling Agent, L-Phenylalanyl-glycyl-glycyl-D-phenylalanine Trihydrate

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Abstract. L-Phenylalanyl-glycyl-glycyl-D-phenylalanine trihydrate, $C_{22}N_4O_5H_{26}.3H_2O$, $M_r = 480{\cdot}5$, monoclinic, $P2_1$, $a = 5{\cdot}787\ (1)$, $b = 11{\cdot}787\ (2)$, $c = 17{\cdot}610\ (2)$ Å, $\beta = 104{\cdot}52\ (1)°$, $V = 1162{\cdot}7\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}372$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 7{\cdot}62$ cm^{-1}, $F(000) = 512$, $T = 283$ K, $R = 0{\cdot}058$ for 1212 unique observed reflections. The molecule has adopted a compact and amphipathic conformation. Peptide torsion angles: L-Phe1: $\psi = -120{\cdot}6\ (9)$, $\omega = -171{\cdot}7\ (8)$, $\chi^1 = 172{\cdot}4\ (9)$, $\chi^{2,1} = 55{\cdot}5\ (10)$; Gly2: $\varphi = -109{\cdot}6\ (9)$, $\psi = -12{\cdot}9\ (9)$, $\omega = 180{\cdot}0\ (8)$; Gly3: $\varphi = -92{\cdot}1\ (7)$, $\psi = 149{\cdot}8\ (8)$, $\omega = -175{\cdot}6\ (7)$; D-Phe4: $\varphi = 73{\cdot}2\ (8)$, $\psi_T^1 = -34{\cdot}2\ (7)$, $\chi^1 = 62{\cdot}7\ (7)$, $\chi^{2,1} = 52{\cdot}9\ (9)°$. Intramolecular edge-to-face interaction between phenyl rings: phenyl(L-Phe1)–phenyl(D-Phe4) centroid separation = 5·12 (1) Å and dihedral angle = 76·9 (7)°. Intermolecular hydrogen bonds: N(L-Phe1)–H···O(Gly2) = 2·853 (10), N(L-Phe1)–H···O(1)(D-Phe4′) = 2·787 (10), N(L-Phe1)–H···O($W2$) = 3·042 (10), O(L-Phe1)···H–O($W3$) = 2·801 (12), N(Gly2)–H···O($W3$) = 2·918 (13), N(Gly3)–H···O($W3$) = 2·979 (13), N(D-Phe4)–H···O2(D-Phe4′) = 2·900 (10), O(2)(D-Phe4)···H–O($W2$) = 2·610 (12), and O($W2$)–O($W3$) = 2·770 (12) Å. Intermolecular edge-to-face interaction between phenyl rings: phenyl(L-Phe1)–phenyl(D-Phe4′) centroid separation = 4·78 (1) Å and dihedral angle = 54·3 (7)°. Finally, there is evidence of static disorder and/or increased thermal motion of waters 1 and 2, and the atoms N(Gly2), CA(Gly2), C(Gly2) and O(Gly2), which may be due to dehydration of water 3 [refined occupancy = 0·31 (2)]. The atoms CA(Gly2) and C(Gly2) make unreasonably short contacts with water 3, and the hydrogen-bonding network in the polar region of the crystal is only partially satisfied.

Experimental. Thin-plate, pseuohexagonal crystal by vapor diffusion from 10% 2-methyl-2,4-pentanediol at neutral pH, 0·5 × 0·4 × 0·08 mm, Nicolet $P3$ diffractometer, Ni-filtered radiation, ω-scan method, $(\sin\theta)/\lambda < 0{\cdot}58$ Å^{-1}, lattice parameters from the 2θ values of 15 reflections with $34 < 2\theta < 45°$, no absorption correction, $h = -6$ to 6, $k = 0$ to 10, $l = 0$ to 20, reflections 202, 036, 141, 115 and $\bar{2}06$ as intensity standards, intensity variation <3%. 2074 unique reflections measured, 862 excluded during refinement [$F < 3\sigma(F)$]. Structure solved by direct methods (*MULTAN*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), first E map revealed the positions of all but four non-H atoms, successive Fourier syntheses located a C atom and three H_2O molecules to

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give a final R factor of 20·5%; least-squares refinement using *SHELX*76 (Sheldrick, 1976), F magnitudes, unit weights; isotropic and then anisotropic temperature factors gave $R = 0{\cdot}058$ and $S = 1{\cdot}02$ with H atoms at positions calculated where possible or located by difference synthesis. 310 parameters varied: x, y, z, U_{ij} for non-H atoms, a single U for all phenyl-ring H atoms, and a single U for all other H atoms. Occupancy varied for H_2O3, final value = 0·31 (2). In final cycle $(\Delta/\sigma)_{max} = 0{\cdot}21$. Final difference synthesis $(\Delta\rho)_{max} = 0{\cdot}17$, $(\Delta\rho)_{min} = -0{\cdot}21$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Table 1* gives the atom parameters. Fig. 1 shows the molecular structure and the water numbering scheme drawn by *ORTEP*II (Johnson, 1976). The tetrapeptide numbering scheme is standard for proteins (IUPAC–IUB Commission on Biochemical Nomenclature, 1970).

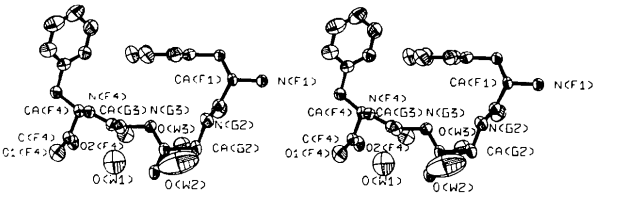

Fig. 1. Stereodrawing of the molecular structure showing the water numbering scheme. The thermal ellipsoids are drawn at the 50% level.

Related literature. The compound was synthesized according to Gorecki, Votano & Rich (1980). Related structures were reported by Wang & Burley (1987) and Burley & Wang (1987*a*,*b*). A mechanism of antigelling was proposed by Burley, Wang, Votano & Rich (1986). The intra- and intermolecular edge-to-face interactions between phenyl rings are enthalpically favorable (Burley & Petsko, 1986).

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43675 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
N(*F*1)	0·5048 (12)	0·0568 (9)	0·1565 (4)	0·039
CA(*F*1)	0·4465 (17)	0·1759	0·1780 (5)	0·040
CB(*F*1)	0·5428 (17)	0·1901 (10)	0·2666 (5)	0·045
CG(*F*1)	0·5225 (16)	0·3119 (11)	0·2925 (5)	0·047
*CD*1(*F*1)	0·7243 (18)	0·3690 (12)	0·3329 (6)	0·059
*CE*1(*F*1)	0·706 (2)	0·4827 (13)	0·3562 (7)	0·075
CZ(*F*1)	0·494 (2)	0·5387 (12)	0·3380 (7)	0·078
*CE*2(*F*1)	0·292 (2)	0·4842 (12)	0·2966 (7)	0·069
*CD*2(*F*1)	0·3011 (17)	0·3694 (11)	0·2744 (6)	0·054
C(*F*1)	0·582 (2)	0·2596 (11)	0·1359 (5)	0·051
O(*F*1)	0·7960 (13)	0·2571 (9)	0·1476 (4)	0·068
N(*G*2)	0·4334 (17)	0·3290 (9)	0·0878 (5)	0·064
CA(*G*2)	0·521 (3)	0·4046 (10)	0·0341 (6)	0·092
C(*G*2)	0·525 (2)	0·5317 (11)	0·0560 (6)	0·063
O(*G*2)	0·5498 (20)	0·6001 (9)	0·0066 (4)	0·099
N(*G*3)	0·4965 (14)	0·5570 (9)	0·1264 (4)	0·043
CA(*G*3)	0·5005 (15)	0·6768 (10)	0·1520 (5)	0·043
C(*G*3)	0·7558 (15)	0·7106 (10)	0·1959 (5)	0·043
O(*G*3)	0·9301 (12)	0·6712 (9)	0·1777 (4)	0·066
N(*F*4)	0·7684 (11)	0·7892 (9)	0·2509 (4)	0·038
CA(*F*4)	1·0056 (13)	0·8338 (10)	0·2926 (5)	0·036
CB(*F*4)	0·9821 (16)	0·9042 (11)	0·3629 (5)	0·047
CG(*F*4)	0·8955 (14)	0·8346 (11)	0·4245 (5)	0·045
*CD*1(*F*4)	0·7035 (17)	0·8756 (12)	0·4520 (6)	0·067
*CE*1(*F*4)	0·632 (2)	0·8143 (16)	0·5103 (7)	0·087
CZ(*F*4)	0·745 (3)	0·7180 (15)	0·5386 (7)	0·091
*CE*2(*F*4)	0·933 (3)	0·6757 (13)	0·5128 (7)	0·084
*CD*2(*F*4)	1·0104 (19)	0·7349 (11)	0·4555 (6)	0·059
C(*F*4)	1·1111 (15)	0·8141 (11)	0·2395 (5)	0·044
O1(*F*4)	0·9725 (12)	0·9752 (9)	0·1908 (4)	0·072
O2(*F*4)	1·3303 (9)	0·9097 (9)	0·2500 (4)	0·052
O(*W*1)	0·0171 (15)	0·7349 (11)	0·0075 (6)	0·105
O(*W*2)	0·975 (2)	0·4966 (19)	0·9504 (7)	0·220
O(*W*3)	0·023 (4)	0·453 (2)	0·1116 (12)	0·072

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