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Structure of a Tripeptide Containing a Dehydro Amino Acid: *tert*-Butoxycarbonylglycyl-dehydrophenylalanyl-glycine Methyl Ester

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Abstract. $C_{19}H_{25}N_3O_6$, $M_r = 391{\cdot}43$, monoclinic, $C2/c$, $a = 39{\cdot}224$ (4), $b = 5{\cdot}6895$ (4), $c = 23{\cdot}926$ (2) Å, $\beta = 128{\cdot}93$ (8)°, $V = 4153{\cdot}4$ (5) Å^3, $Z = 8$, $D_x = 1{\cdot}252$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0{\cdot}417$ mm^{-1}, $F(000) = 1664$. Final $R = 0{\cdot}044$ for 3068 observed reflections measured on a diffractometer. The molecules in the crystal form a two-dimensional net by means of two intermolecular hydrogen bonds. The peptide chain adopts a type II β turn with an N(4)···O(1) intramolecular hydrogen bond. The torsional angles φ and ψ for dehydrophenylalanine are −69·3 (2) and −11·4 (2)°, respectively.

Introduction. Incorporation of a dehydro amino acid into a peptide decreases its conformational flexibility and has a stabilizing effect on a β turn (Aubry, Boussard & Marraud, 1984), similar to that of proline. Also the kind of neighbouring amino acids plays an important role in peptide chain conformation. The crystal structure of the protected tripeptide glycyl-dehydrophenylalanyl-glycine is reported here as part of a program of X-ray studies of α,β-unsaturated oligopeptides (Główka, Gilli, Bertolasi & Makowski, 1987; Galdecki, 1986). Boc-Gly-ΔPhe-Gly-OMe represents an example of a peptide with a rigid central amino acid (ΔPhe) placed between two flexible glycine residues; thus the conformational preference of dehydrophenylalanine can be easily revealed. Smith & Pease (1980) noticed frequent occupancy of $i+1$ and $i+2$ positions in a β turn by glycine. So far a β turn has been reported in the crystals of Z-Phe-ΔPhe (Główka, Gilli, Bertolasi & Makowski, 1987) and Z-Phe-ΔPhe-Gly-OMe (Galdecki, 1986) though for N-Ac-ΔPhe-ΔPhe-Gly (Pieroni, Montagnoli, Fissi, Merlino & Ciardelli, 1975) a β-pleated sheet structure was found. In three saturated oligopeptides containing Phe-Gly or Gly-Phe (or both) fragment(s), a β turn was also observed [Tyr-Gly-Gly-Phe, Prange & Pascard (1979); Boc-Gly-Gly-Phe, Ishida, Tanabe & Inoue (1983) and Tyr-Gly-Gly-Phe-Leu, Smith & Griffin (1978)]. On the other hand there is an equal number of acyclic oligopeptides with other than reverse-turn conformations: Gly-Gly-Phe-Leu (Prange & Pascard, 1979); Boc-Gly-Phe (Murali, Subramanian & Parthasarathy, 1986) and Gly-Phe-Gly (Marsh & Glusker, 1961).

Experimental. The compound was synthesized by Dr M. Makowski of the Pedagogical University in Opole, Poland, and recrystallized from 2-propanol–tetrahydrofuran (3:1) solution. Data collection: CAD-4F, Cu $K\alpha$, 0·34 × 0·22 × 0·10 mm; cell parameters from 25 reflections ($25 < \theta < 32°$); 3910 unique reflections measured ($h_{max} = \pm 47$, $k_{max} = 6$, $l_{max} = 29$) in $\omega/2\theta$ scan mode, $\theta_{max} = 70°$; three standard reflections monitored every 2000 s, 5% drop in intensity during data collection, 3068 observed reflections [$F_o > 2{\cdot}5\sigma(F_o)$], Lp correction, absorption neglected; direct methods [*MULTAN*78 of Main, Hull, Lessinger, Germain, Declercq & Woolfson (1978)], anisotropic refinement on F, H atoms isotropic, final cycle 353 parameters, $(\Delta/\sigma)_{max} = 1{\cdot}3$ in x for H(221), $(\Delta/\sigma)_{mean} = 0{\cdot}1$, $R = 0{\cdot}044$, $wR = 0{\cdot}047$, $S = 1{\cdot}03$, $w^{-1} = \sigma^2(F_o) + 0{\cdot}0001(F_o)^2$; final ΔF showed $\rho_{max} = 0{\cdot}14$ e Å^{-3}.

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Other programs used: *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *PLUTO* (Motherwell, 1979). The final atomic parameters are given in Table 1.*

Discussion. Numbering scheme of the atoms and a general view of the molecule are shown in Fig. 1, while the bond lengths and angles are given in Table 2. All values are in agreement with those found in similar oligopeptides. The most unusual are C(9)=C(10)–C(11) and C(10)–C(11)–C(16) bond angles of 132·2 (2) and 125·0 (2)°, which are characteristic of ΔPhe residues as analogous angles in Z-Phe-ΔPhe (Głowka, Gilli, Bertolasi & Makowski, 1987) are 131·8 (2) and 124·8 (2)°, respectively. The tripeptide forms a type II β turn (Venkatachalam, 1968) with an N(18)–H···O(04) intramolecular hydrogen bond between the third and the first peptide unit. The N···O distance is 2·984 (3) and C(06)···C(19) [Cα(1)···Cα(3)] distance is 5·387 (4) Å, which agree well with

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44956 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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the values found by Venkatachalam (1968). The coplanarity of the first and third peptide groups (Gly) and perpendicular orientation of the second (Fig. 1) are also characteristic of oligopeptide fragments within β turns. Both glycine residues adopt a conformation known as a polyglycine helix (Walton, 1981) with φ and ψ close to 80 and $-150°$ (Table 2). The conformation of the unsaturated peptide (ΔPhe) is close to an α-helix [$\varphi_2 = -69{\cdot}3$ (2), $\psi_2 = -11{\cdot}4$ (2)°] and the side-chain parameters are $\chi_1 = -2{\cdot}1$ (3) and $\chi_2 = -2{\cdot}2$ (3)° due to conjugation.

In the crystal the molecules of Boc-Gly-ΔPhe-Gly-OMe form a two-dimensional net utilizing two intermolecular hydrogen bonds (Table 2). One bond,

Table 1. *Fractional atomic coordinates* (× 10^5) *and equivalent isotropic* (× 10^2) *temperature factors* (Å^2) *for non-*H *atoms*

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

	x	y	z	B_{eq}
C(1)	77761 (9)	−34250 (42)	63294 (14)	734 (15)
C(2)	79309 (6)	−9167 (37)	63966 (11)	488 (10)
C(3)	77610 (8)	1344 (46)	56811 (12)	709 (13)
O(3)	77966 (4)	5293 (23)	67353 (6)	406 (6)
C(4)	73710 (5)	8457 (31)	64254 (9)	335 (7)
O(4)	70596 (4)	2109 (24)	58188 (6)	404 (6)
C(5)	84251 (8)	−7178 (55)	69400 (15)	813 (16)
N(5)	73352 (4)	19495 (26)	68793 (7)	343 (6)
C(6)	69040 (5)	23645 (31)	66627 (9)	330 (7)
C(7)	66528 (5)	559 (30)	64596 (8)	295 (7)
O(7)	68269 (4)	−17679 (21)	67837 (6)	352 (5)
N(8)	62204 (4)	1867 (23)	58929 (7)	290 (6)
C(9)	59499 (5)	−18586 (28)	56210 (8)	278 (7)
C(10)	56234 (5)	−22149 (30)	56454 (9)	336 (7)
C(11)	54586 (5)	−8252 (33)	59460 (9)	356 (8)
C(12)	50935 (6)	−16647 (38)	58528 (10)	454 (9)
C(13)	49159 (6)	−4683 (45)	61172 (12)	555 (11)
C(14)	50982 (7)	15942 (46)	64837 (12)	568 (12)
C(15)	54594 (7)	24753 (42)	65798 (13)	619 (12)
C(16)	56387 (7)	12908 (39)	63149 (12)	565 (11)
C(17)	60280 (5)	−36241 (30)	52531 (9)	299 (7)
O(17)	58571 (4)	−55959 (20)	50869 (7)	374 (6)
N(18)	62869 (5)	−29910 (27)	50939 (8)	431 (7)
C(19)	63970 (6)	−46514 (38)	47735 (10)	469 (9)
C(20)	60147 (7)	−51950 (40)	39999 (11)	465 (10)
O(20)	57194 (5)	−39299 (33)	35894 (9)	675 (9)
O(21)	60657 (5)	−73178 (28)	38320 (8)	630 (9)
C(22)	57281 (9)	−80977 (54)	30933 (14)	838 (17)

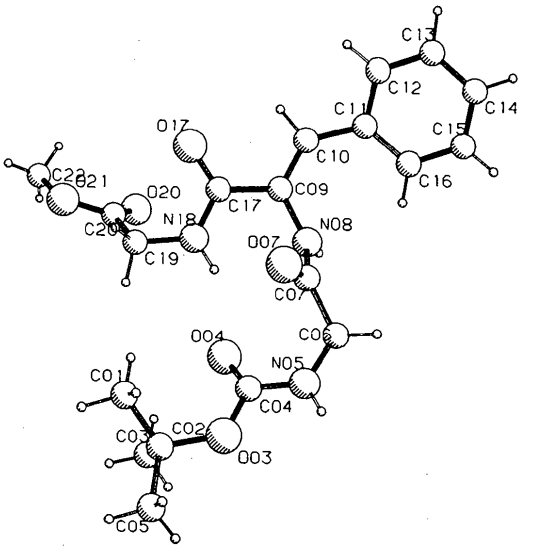

Fig. 1. A view of the title compound (*PLUTO*) and numbering of atoms.

Table 2. *Bond lengths* (Å), *valency and selected torsional angles* (°) *and hydrogen bonds*

C(1)–C(2)	1·519 (3)	C(10)–C(11)	1·464 (4)	C(1)–C(2)–C(3)	112·8 (2)	C(9)–C(10)–C(11)	132·2 (2)
C(2)–C(3)	1·516 (4)	C(11)–C(12)	1·388 (3)	C(1)–C(2)–O(3)	109·1 (3)	C(10)–C(11)–C(12)	117·7 (2)
C(2)–O(3)	1·465 (3)	C(11)–C(16)	1·394 (3)	C(1)–C(2)–C(5)	111·8 (2)	C(10)–C(11)–C(16)	125·0 (2)
C(2)–C(5)	1·515 (3)	C(12)–C(13)	1·379 (4)	C(3)–C(2)–O(3)	110·3 (2)	C(12)–C(11)–C(16)	117·4 (2)
O(3)–C(4)	1·347 (3)	C(13)–C(14)	1·367 (3)	C(3)–C(2)–C(5)	110·9 (3)	C(11)–C(12)–C(13)	121·6 (2)
C(4)–O(4)	1·225 (2)	C(14)–C(15)	1·379 (4)	O(3)–C(2)–C(5)	101·2 (2)	C(12)–C(13)–C(14)	120·4 (3)
C(4)–N(5)	1·336 (3)	C(15)–C(16)	1·382 (5)	C(2)–O(3)–C(4)	121·5 (1)	C(13)–C(14)–C(15)	119·2 (3)
N(5)–C(6)	1·444 (3)	C(17)–O(17)	1·237 (2)	O(3)–C(4)–O(4)	125·5 (2)	C(14)–C(15)–C(16)	120·8 (2)
C(6)–C(7)	1·527 (2)	C(17)–N(18)	1·339 (3)	O(3)–C(4)–N(5)	110·0 (1)	C(11)–C(16)–C(15)	120·7 (3)
C(7)–O(7)	1·216 (2)	N(18)–C(19)	1·443 (3)	O(4)–C(4)–N(5)	124·5 (2)	C(9)–C(17)–O(17)	122·0 (2)
C(7)–N(8)	1·353 (2)	C(19)–C(20)	1·511 (3)	C(4)–N(5)–C(6)	118·9 (1)	C(9)–C(17)–N(18)	117·5 (2)
N(8)–C(9)	1·427 (2)	C(20)–O(20)	1·181 (3)	N(5)–C(6)–C(7)	110·5 (2)	O(17)–C(17)–N(18)	120·5 (2)
C(9)–C(10)	1·333 (3)	C(20)–O(21)	1·327 (3)	C(6)–C(7)–O(7)	122·7 (1)	C(17)–N(18)–C(19)	120·6 (2)
C(9)–C(17)	1·489 (3)	O(21)–C(22)	1·460 (3)	C(6)–C(7)–N(8)	115·1 (1)	N(18)–C(19)–C(20)	112·8 (2)
				O(7)–C(7)–N(8)	122·3 (2)	C(19)–C(20)–O(20)	126·4 (2)
				C(7)–N(8)–C(9)	121·1 (1)	C(19)–C(20)–O(21)	109·6 (2)
				N(8)–C(9)–C(10)	124·3 (2)	O(20)–C(20)–O(21)	124·0 (2)
				N(8)–C(9)–C(17)	116·7 (2)	C(20)–O(21)–C(22)	116·6 (2)
				C(10)–C(9)–C(17)	118·9 (2)		

O(3)–C(4)–N(5)–C(6)	(ω_0')	−177·2 (2)	C(9)–C(17)–N(18)–C(19)	ω_2	176·6 (1)
C(4)–N(5)–C(6)–C(7)	φ_1	56·3 (2)	C(17)–N(18)–C(19)–C(20)	φ_3	71·7 (2)
N(5)–C(6)–C(7)–N(8)	ψ_1	−142·0 (2)	N(18)–C(19)–C(20)–O(21)	(ψ_3')	−153·8 (2)
C(6)–C(7)–N(8)–C(9)	ω_1	176·8 (2)	N(8)–C(9)=C(10)–C(11)	χ_1	−2·1 (3)
C(7)–N(8)–C(9)–C(17)	φ_2	−69·3 (2)	C(9)=C(10)–C(11)–C(16)	χ_2	−2·2 (3)
N(8)–C(9)–C(17)–N(18)	ψ_2	−11·4 (2)			

X–H···Y	X–H(Å)	X···Y (Å)	H···Y (Å)	X–H···Y (°)	Symmetry code for Y
N(5)–H···O(7)	0·903 (14)	2·890 (4)	1·992 (14)	173 (3)	1·5−x, 0·5+y, 1·5−z
N(8)–H···O(17)	0·858 (17)	2·838 (2)	1·980 (17)	179 (2)	x, 1+y, z
N(18)–H···O(4)	0·895 (18)	2·984 (3)	2·178 (19)	150 (2)	x, y, z

N(08)···O(17) links equivalent molecules in neighbouring cells (x, $y\pm1$, z) while the other, N(05)··· O(07), spans molecules which belong to chains transformed by a 2_1 axis.

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Structure and Stereochemistry of 7β-[(+)-Camphorsulfonyl]-9α-hydroxylongipin-2-en-1-one*

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Abstract. 7β-[(+)-7,7-Dimethyl-2-oxobicyclo[2.2.1]-heptane-1-methanesulfonyl]-9α-hydroxylongipin-2-en-1-one, $C_{25}H_{36}O_6S$, $M_r = 464{\cdot}6$, monoclinic, $P2_1$, $a = 7{\cdot}195$ (4), $b = 11{\cdot}128$ (4), $c = 15{\cdot}003$ (4) Å, $\beta = 98{\cdot}45$ (4)°, $V = 1188$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}30$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}166$ mm^{-1}, $F(000) = 500$, $T = 293$ K, $R = 0{\cdot}073$ for 1490 observed reflections. The X-ray study confirms that in the solid state the structure and absolute configuration of the title compound are as inferred from chemical and spectroscopic evidence. The cyclohexenone and cyclobutane rings have 1,2-diplanar and normal puckered conformations, respectively. The cycloheptane ring adopts a twist-chair conformation. The geometry and dimensions of the camphor ring system are similar to those in related molecules. The crystal structure is stabilized by an intermolecular hydrogen bond.

Introduction. The genus *Stevia* (Compositae) is abundant in Mexico. Some of these plants are used in folk medicine (Altschul, 1975) and as a sweetening agent (Soejarto, Compadre, Medon, Kamath & Kinghorn, 1983). The chemical investigation of the Mexican *Stevia* species showed the occurrence of longipinenes (Román *et al.*, 1985). The longipinene derivative (1) was isolated from the dried and ground roots of *Stevia lucida* Lay, var. *lucida*, collected in the Cubilete mountain, located in the State of Guanajuato, Mexico. Chemical and spectroscopic studies led to the

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