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The Crystal Structure of *tert*-Butyloxycarbonyl-L-prolyl-L-leucylglycine Hydrate

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Crystals of the title compound are monoclinic, $P2_1$, with $a = 10 \cdot 036$ (1), $b = 18 \cdot 142$ (2), $c = 6 \cdot 191$ (1) Å, $\beta = 101 \cdot 77$ (2)°, $Z = 2$. The final R is $0 \cdot 037$ for 1498 non-zero reflexions. The peptide molecule is folded into a β-turn of type I, in which Pro and Leu are at the corner and an intramolecular hydrogen bond is formed between NH of Gly and CO of the oxycarbonyl group. The folding is essentially the same as that found in some peptides having an X-Pro-Leu-Gly- sequence (X: any acyl group). Two common rules in the foldings of peptides are found: (i) the $NC^\alpha C'$ angle of the second residue, Pro in this peptide, in the four residues involved in the β-turn of type I is extraordinarily larger than the $NC^\alpha C'$ angles of the residues having other conformations; (ii) the most probable conformation of the Leu residues in peptides has a *trans* zigzag chain of $C^{\delta 1}-C^\gamma-C^\beta-C^\alpha-C'$.

Introduction

The X-ray studies have shown that, although only a few linear oligopeptides with three or more amino acid residues have so far been obtained as single crystals suitable for X-ray experiments, most of these peptides are folded into one of three structures, β-sheet, polyproline II type helix and β-turn. In particular, all those having the X-Pro-Leu-Gly- sequence (X: any acyl group) are folded into the β-turn conformation.

The crystal structures of a series of oligopeptides, benzyloxycarbonyl(Z)-Gly-Pro (Tanaka, Kozima, Ashida, Tanaka & Kakudo, 1977), Z-Gly-Pro-Leu (Yamane, Ashida, Shimonishi, Kakudo & Sasada, 1976), Z(p-Br)-Gly-Pro-Leu-Gly (Ueki, Ashida, Kakudo, Sasada & Katsube, 1969), Z(o-Br)-Gly-Pro-Leu-Gly-Pro (Ueki, Bando, Ashida & Kakudo, 1971) and Z-Gly-Pro-Leu-Gly-Pro (Bando, Tanaka, Ashida & Kakudo, 1973), have been determined, the last two pentapeptides having a substrate specificity for the enzyme collagenase. In this series each member has its own characteristic structural feature; the dipeptide has a β-sheet-type hydrogen bond, the tripeptide has a *cis* peptide bond at the Gly-Pro linkage, and the tetra- and

pentapeptides are folded at the Pro-Leu parts into the typical β-turn of type I [hereafter abbreviated as β-I turn (Venkatachalam, 1968)]. The structures of a few more peptides with a similar sequence have also been reported; S-benzyl-Cys-Pro-Leu-Gly-NH_2 (Rudko & Low, 1975) has a β-I turn at the Pro-Leu part, and Pro-Leu-Gly-NH_2 (Reed & Johnson, 1973) has a β-II turn with Leu-Gly at the corner.

The present peptide, *tert*-butyloxycarbonyl(Boc)-Pro-Leu-Gly, is therefore expected to fold into a β-I turn conformation. In this conformation, however, the C=O bond of Boc and the N—C^α bond of Pro should be *cis*, contrary to the *trans* arrangement found in all the Boc (or *tert*-amyloxycarbonyl)-Pro structures reported so far (Matsuzaki, 1974; Benedetti, Ciajolo & Maisto, 1974; Kartha, Ashida & Kakudo, 1974; Robert 1976).

Experimental

Crystal data

tert-Butyloxycarbonyl-L-prolyl-L-leucylglycine hydrate (needle crystal from an ethyl acetate–hexane solution), $C_{18}H_{31}N_3O_7$, $M_r = 401 \cdot 46$. Monoclinic, $P2_1$,

$a = 10 \cdot 036$ (1), $b = 18 \cdot 142$ (2), $c = 6 \cdot 191$ (1) Å, $\beta = 101 \cdot 77$ (2)°, $U = 1103 \cdot 5$ Å^3, $D_m = 1 \cdot 208$, $D_c = 1 \cdot 214$ g cm^{-3}, $Z = 2$, $F(000) = 432$. $\mu(\text{Cu } K\alpha) = 8 \cdot 95$ cm^{-1}.

Intensity measurements

Intensity measurements were made on a Rigaku four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation, ω–2θ scan with range $\Delta(2\theta) = (1 \cdot 4 + 0 \cdot 15 \tan \theta)°$ and speed $2°$ min^{-1}, and background counts for 10 s each at both ends of the scan. 1563 reflexions with $2\theta < 115°$ were collected, of which 1498 were non-zero. Lorentz and polarization factors were applied, but no absorption corrections were made. The crystal size was $0 \cdot 3 \times 0 \cdot 2 \times 0 \cdot 16$ mm.

Structure determination

The crystal structure was solved by the direct method with the program *MULTAN* (Germain, Main & Woolfson, 1971). The parameters were refined by the block-diagonal least-squares method (*HBLSV*: Ashida, 1973), the H atoms being included in the refinement. The final R value was $0 \cdot 042$ for all the reflexions, and $0 \cdot 037$ if 65 zero reflexions were omitted. A few strong reflexions suffered seriously from extinction, but no correction was tried. The atomic scattering factors were

Table 1. *The atomic positional parameters, with their e.s.d.'s in parentheses* ($\times 10^4$)

	x	y	z
C(1)	−858 (3)	3153 (2)	1268 (5)
C(2)	1452 (3)	3761 (2)	1533 (6)
C(3)	−177 (3)	3658 (2)	−2086 (5)
C(4)	327 (3)	3309 (2)	121 (5)
O(1)	890 (2)	2604 (1)	−473 (3)
C(5)	1440 (2)	2116 (1)	1049 (4)
O(2)	1607 (2)	2189 (1)	3044 (3)
N(1)	1836 (2)	1500 (1)	98 (3)
C(6)	2294 (2)	846 (1)	1428 (4)
C(7)	2462 (3)	279 (1)	−324 (5)
C(8)	1375 (3)	489 (2)	−2284 (5)
C(9)	1440 (3)	1322 (2)	−2273 (5)
C(10)	3591 (2)	936 (1)	3139 (4)
O(3)	3849 (2)	503 (1)	4705 (3)
N(2)	4425 (2)	1487 (1)	2872 (3)
C(11)	5670 (2)	1662 (1)	4453 (4)
C(12)	6914 (3)	1657 (1)	3390 (5)
C(13)	7150 (3)	929 (2)	2310 (5)
C(14)	7447 (4)	305 (2)	3960 (8)
C(15)	8305 (3)	1026 (2)	1032 (8)
C(16)	5523 (2)	2393 (1)	5597 (4)
O(4)	6522 (2)	2765 (1)	6437 (3)
N(3)	4268 (2)	2598 (1)	5752 (3)
C(17)	4030 (3)	3285 (2)	6791 (4)
C(18)	4671 (2)	3301 (1)	9226 (4)
O(5)	4740 (2)	2776 (1)	10413 (3)
O(6)	5109 (2)	3957 (1)	9875 (3)
W(1)	6474 (2)	4082 (1)	3902 (3)

Table 2. *Hydrogen positional parameters, with their e.s.d.'s in parentheses* ($\times 10^3$)

	x	y	z
H(11)	−158 (3)	291 (2)	7 (6)
H(12)	−121 (3)	361 (2)	160 (5)
H(13)	−49 (3)	299 (2)	279 (5)
H(21)	222 (3)	380 (2)	63 (5)
H(22)	186 (3)	363 (2)	328 (5)
H(23)	115 (3)	424 (2)	165 (6)
H(31)	63 (2)	374 (1)	−286 (4)
H(32)	−71 (3)	336 (2)	−302 (5)
H(33)	−65 (3)	409 (2)	−198 (5)
H(61)	158 (2)	71 (1)	227 (3)
H(71)	340 (3)	31 (2)	−75 (5)
H(72)	242 (3)	−19 (2)	30 (5)
H(81)	148 (2)	28 (2)	−363 (4)
H(82)	40 (3)	32 (2)	−195 (5)
H(91)	51 (3)	160 (2)	−284 (6)
H(92)	215 (3)	157 (2)	−305 (5)
H(N21)	428 (3)	179 (2)	169 (5)
H(111)	579 (3)	129 (1)	567 (4)
H(121)	770 (2)	178 (1)	468 (4)
H(122)	683 (3)	205 (2)	241 (5)
H(131)	622 (3)	73 (2)	115 (5)
H(141)	678 (4)	25 (3)	502 (7)
H(142)	829 (4)	46 (3)	481 (7)
H(143)	751 (4)	−20 (3)	315 (8)
H(151)	846 (3)	50 (2)	40 (6)
H(152)	916 (4)	119 (2)	220 (8)
H(153)	814 (4)	146 (3)	−26 (7)
H(N31)	363 (2)	238 (1)	503 (4)
H(171)	303 (2)	333 (2)	689 (4)
H(172)	436 (2)	370 (1)	614 (4)
H(O61)	560 (3)	397 (1)	1143 (4)
H(W1)	630 (3)	447 (2)	473 (6)
H(W2)	656 (3)	379 (2)	484 (5)

taken from *International Tables for X-ray Crystallography* (1974). The function minimized was $\Sigma w(\Delta F)^2$, with $w = 0 \cdot 6$ for $|F_o| = 0$, and $w = [\sigma^2(F) - 0 \cdot 056|F_o| + 0 \cdot 004|F_o|^2]^{-1}$ for $|F_o| > 0$, where $\sigma(F)$ is the standard deviation based on counting statistics. All the calculations were made on the FACOM 230-60 computer of Nagoya University. The final positional parameters are listed in Tables 1 and 2.*

Discussion

The bond lengths and angles are shown in Fig. 1. Some bond angles are seriously affected by the non-bonded interactions. The torsion angles, defined by the IUPAC–IUB Commission on Biochemical Nomenclature (1970), are also shown in Fig. 1. An

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* Lists of the temperature factors, anisotropic for non-hydrogen atoms and isotropic for H atoms, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32628 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ORTEP drawing (Johnson, 1965) of a molecule is shown in Fig. 2. The equations of the best planes of several planar groups are listed in Table 3.
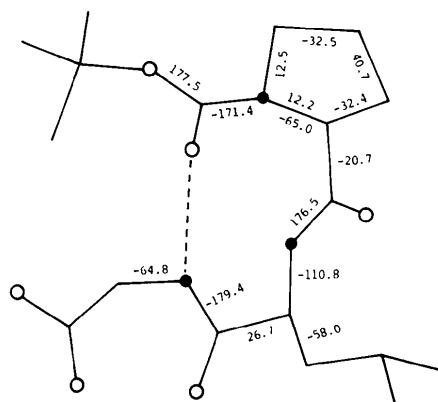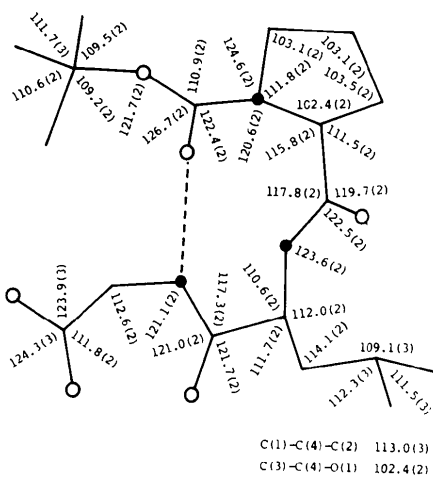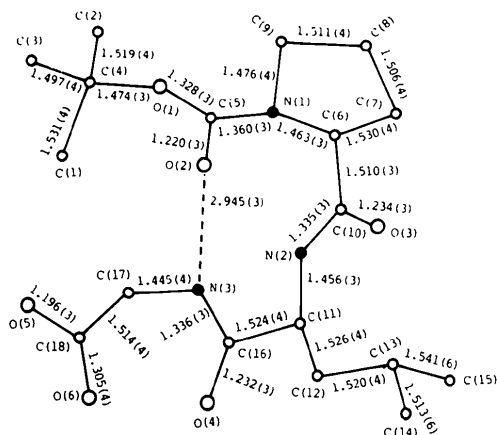

C(1)–C(4)–C(2)   113.0(3)
C(3)–C(4)–O(1)   102.4(2)

Fig. 1. Bond lengths (Å), angles (°) and torsion angles (°).

Table 3. *Best planes*

(*a*) Equations. $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$.

(I) $-0.9374X - 0.3479Y + 0.0159Z = -2.5430$ Boc-Pro amide
(II) $0.6067X - 0.5925Y - 0.5300Z = -0.0762$ Pro-Leu peptide
(III) $0.0984X + 0.4843Y - 0.8693Z = -0.3855$ Leu-Gly peptide
(IV) $-0.9522X + 0.2258Y + 0.2059Z = -0.8440$ Gly carboxyl
(V) $-0.9509X - 0.2291Y + 0.2083Z = -2.3413$ Pro ring

(*b*) Displacements ($\times 10^3$ Å) of atoms from the planes

(I)		(II)		(III)	
O(1)	2	C(6)	−5	C(11)	4
C(5)	−13	C(10)	7	C(16)	15
O(2)	40	O(3)	7	O(4)	−13
N(1)	−118	N(2)	29	N(3)	−12
C(6)	33	C(11)	−30	C(17)	8
C(9)	63	H(N21)*	81	H(N31)*	125

(IV)		(V)	
C(17)	2	N(1)	−10
C(18)	−7	C(6)	152
O(5)	3	C(7)	−204
O(6)	2	C(8)	263
H(O61)*	−85	C(9)	−142
		C(10)*	−702

(*c*) Dihedral angles (°) between the planes

(I)–(V)	13.0	(I)–(II)	111.8
(II)–(III)	76.5	(III)–(IV)	99.4

* Atoms not included in the calculation of the planes.

β-Turn

The main-chain folding, which is characterized by the *β*-I turn, is essentially the same as that found in Z(*p*-Br)-Gly-Pro-Leu-Gly (Ueki *et al.*, 1969), Z(*o*-Br)-Gly-Pro-Leu-Gly-Pro (Ueki *et al.*, 1971), Z-Gly-Pro-Leu-Gly-Pro (Bando *et al.*, 1973) and S-benzyl-Cys-Pro-Leu-Gly-NH$_2$ (Rudko & Low, 1975). Thus it has been shown that all the linear oligopeptides having the *X*-Pro-Leu-Gly-sequence (*X*: any acyl group) are folded at the Pro-Leu part into the *β*-I turn with the intramolecular hydrogen bond between NH of Gly and C=O of *X*. The mean torsion angles (*φ*, *ψ*) of these peptides are (−64.1, −24.7°) for Pro and (−106.6, 12.7°) for Leu.

In order to compare these *β*-I turns in detail, for each pair of peptides the atomic coordinates of one peptide were fitted to those of the other by adjusting the relative positional and orientational parameters by a least-squares procedure; the quantity minimized was $\Delta_{ij}^2 = \Sigma_k (|r_{ik} - r_{jk}|)^2$, where r_{ik} and r_{jk} are the positional vectors of the *k*th atoms in the *i*- and *j*th peptides, and the summation was made over nine non-hydrogen atoms in the hydrogen-bonded loop of the *β*-I turn and five others directly bonded to the atoms in the loop. The root-mean-square deviations, Δ_{ij}, are 0.089–0.180 Å for group *A* [Z(*p*-Br)-Gly-Pro-Leu-Gly, Z(*o*-Br)-Gly-Pro-Leu-Gly-Pro, Z-Gly-Pro-Leu-Gly-Pro and the present peptide], 0.117 Å for group *B* (two molecules

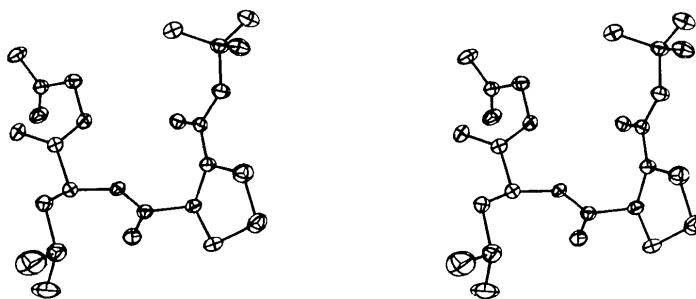Fig. 2. A stereodrawing of a molecule. The thermal ellipsoids are scaled to include 30% probability.

of S-benzyl-Cys-Pro-Leu-Gly-NH$_2$), and 0·372–0·474 Å between A and B. The similarity of the conformations within each group is striking, while the dissimilarity between the two groups is small but significant, and is a cause or effect of the different conformations of the side chains in the two groups.

The NC$^{\alpha}$C' angle of Pro, 115·8°, in this peptide is extraordinarily larger than usual. This is a common characteristic of the NC$^{\alpha}$C' angle of the second residues in the β-I turn, the mean angles being 115·1° for nine Pro residues and 113·6° for eight non-Pro residues,[*] while the mean NC$^{\alpha}$C' angle in peptides given by Marsh & Donohue (1967) is 111°, and the mean for about 20 Pro residues having other conformations is 110·5°. This widening of the angle in the β-I turn, which is due to the steric repulsion between the carbonyl group of the first residue and the peptide group joining the second and third residues, should be taken into account in the model building and refinement of the protein structures. On the other hand, no such widening of the angle is observed in the β-II turn, the mean for three structures being 111·3°.

Pyrrolidine ring

The conformation of the pyrrolidine ring is very similar to those in the β-turns of group A, but is different from those in group B. Following the notation of the pyrrolidine-ring conformation in peptides (Ashida & Kakudo, 1974), the rings in group A are C_2–C$^{\nu}$-exo in the present peptide and $Z(p$-Br)-Gly-Pro-Leu-Gly, C_s–C$^{\beta}$-endo in $Z(o$-Br)-Gly-Pro-Leu-Gly-Pro and C_s–C$^{\nu}$-exo in Z-Gly-Pro-Leu-Gly-Pro;

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* The mean values were obtained from the following structures: for Pro in the β-I turn, $Z(p$-Br)-Gly-Pro-Leu-Gly, $Z(o$-Br)-Gly-Pro-Leu-Gly-Pro, Z-Gly-Pro-Leu-Gly-Pro, S-benzyl-Cys-Pro-Leu-Gly-NH$_2$, Boc-Pro-Leu-Gly, Boc-Pro-Pro-Gly-NH$_2$ (Tanaka, Ashida, Shimonishi & Kakudo, 1977), and cyclochlorotine (Yoshioka, Nakatsu, Sato & Tatsuno, 1973); for non-Pro in the β-I turn, Li antamanide (Karle, 1974a), Na antamanide (Karle, 1974b) tuberactinomycin O (Yoshioka et al., 1971), tuberactinimycin N (Yoshioka & Nakatsu, 1976), and cyclo(Gly$_4$-Ala$_2$) (Karle, Gibson & Karle, 1970); for the β-II turn, Pro-Leu-Gly-NH$_2$, ferrichrome A (Zalkin, Forrester & Templeton, 1966), and isobutyl-Pro-Ala-isopropylamide (Aubry, 1976).

these three conformations are very close to each other and between them no significant potential energy barrier exists. The conformations in the two molecules of S-benzyl-Cys-Pro-Leu-Gly-NH$_2$ are C_s–C$^{\nu}$-endo. The potential barrier between C$^{\nu}$-exo (and C$^{\beta}$-endo) and C$^{\nu}$-endo is significant.

Leu side chain

In all the Leu residues in group A, C$^{\delta 1}$–C$^{\nu}$–C$^{\beta}$–C$^{\alpha}$–C' is trans zigzag, while in group B C$^{\delta 2}$–C$^{\nu}$–C$^{\beta}$–C$^{\alpha}$–C' is trans zigzag in one molecule and C$^{\delta 2}$–C$^{\nu}$–C$^{\beta}$–C$^{\alpha}$–N is trans zigzag in the other. In almost all the other peptides C$^{\delta 1}$–C$^{\nu}$–C$^{\beta}$–C$^{\alpha}$–C' is trans zigzag: Z-Gly-Pro-Leu (Yamane et al., 1976), Pro-Leu-Gly-NH$_2$ (Reed & Johnson, 1973), Leu-Pro-Gly (Leung & Marsh, 1958), ilamycin B$_1$ (Iitaka, Nakamura, Takada & Takita, 1974), cyclo-Pro-Leu (Karle, 1972), and acetyl-Leu-ethylamide and acetyl-Leu-isopropylamide (Aubry, 1976). An exception is benzoyl-Leu-Gly ethyl ester (Timmins, 1975) in which C$^{\delta 2}$–C$^{\nu}$–C$^{\beta}$–C$^{\alpha}$–C' is trans zigzag. Thus Leu in the peptides usually prefers the trans zigzag C$^{\delta 1}$–C$^{\nu}$–C$^{\beta}$–C$^{\alpha}$–C' chain; that is, the conformation of Leu as found in the present crystal may be the most common one in proteins.

Boc–Pro bond

With respect to the C(5)–N(1) amide bond the two bonds O(1)–C(5) and N(1)–C(6) are trans. This is unique, since the two bonds are cis in all the other Boc(Aoc)-Pro structures reported so far: Boc-(Pro)$_4$ benzyl ester (Matsuzaki, 1974), Boc-Pro (Benedetti et al., 1974), Aoc-(Pro)$_3$ (Kartha et al., 1974), Boc-thiazolidine-4-carboxylic acid (Robert, 1976). The conformational potential energies of the Boc-Pro structures were estimated by a method analogous to that of Levitt & Lifson (1969). The result shows that the bond in question usually prefers the cis form to the trans, the former being more stable than the latter by 1–2 kcal mol^{-1}. Since the energy difference is not very large, the trans form, having a hydrogen bond of medium strength at the C=O group, may be more stable than the cis form, which has no hydrogen bond.

In the present peptide the *trans* form is stabilized by forming an intramolecular $N(3)-H(31)\cdots O(2)$ hydrogen bond which is of essential importance for the β-turn.

The bond angles around the $N(1)$ atom of the pyrrolidine ring depend strongly on the configuration, *cis* or *trans*, of the $C(5)-N(1)$ amide bond. The bond angle $C(5)-N(1)-C(6)$ is $3\cdot5°$ smaller, and the $C(5)-N(1)-C(9)$ angle $3\cdot5°$ larger than their corresponding mean angles, $124\cdot1$ and $121\cdot1°$ respectively, in the *cis* form of the compounds: Boc-(Pro)$_4$ benzyl ester, Boc-Pro, Aoc-(Pro)$_3$, Boc-Pro-Pro-Gly-NH$_2$ (Tanaka *et al.*, 1977). A similar but more exaggerated deformation has been found in the *cis* peptide bonds in the Gly-Pro structure (Yamane *et al.*, 1976) and in small cyclic peptides (*e.g.* Kartha & Ambady, 1975). Through this deformation of the angles the non-bonded interactions around the C^δ atom in the *cis* form are nearly identical with those around the C^α atom in the *trans* form.

Boc group

The $C(3)-C(4)-O(1)$ angle of $102\cdot5°$ is extraordinarily compressed from the regular sp^3 angle, and, owing to this compression, all the $C-C-C$ angles around the $C(4)$ atom are widened by 2 or 3°, releasing the close contacts among the methyl groups. In the ester group the angles $C(4)-O(1)-C(5)$, $121\cdot7°$, and $O(1)-C(5)-O(2)$, $126\cdot7°$, are much larger than their corresponding angles in many other ester groups, *e.g.*
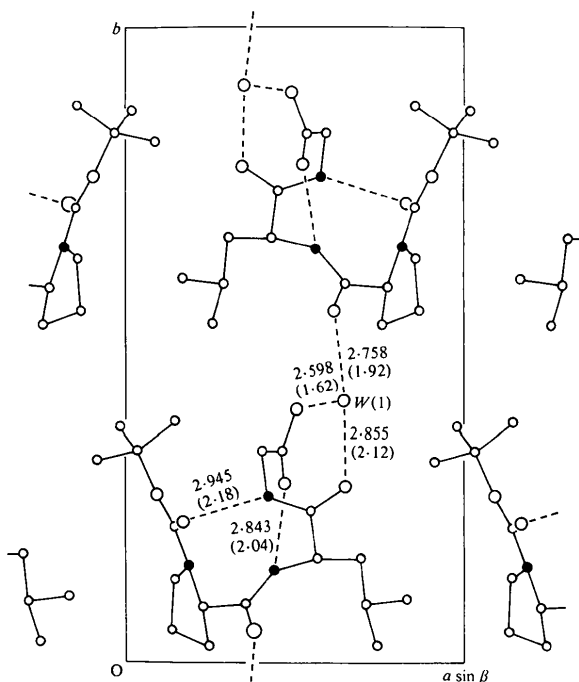
Table 4. *Hydrogen bonds*

Donor Acceptor	$D\cdots A$	$H\cdots A$	$\angle DHA$
$N(3)\cdots O(2)$	2·945 Å	2·18 Å	160°
$N(2)\cdots O(5)^i$	2·843	2·04	147
$O(6)\cdots W(1)^{ii}$	2·598	1·62	173
$W(1)\cdots O(4)$	2·855	2·12	160
$W(1)\cdots O(3)^{iii}$	2·758	1·92	153

Symmetry code

(i) $x, y, -1 + z$
(ii) $x, y, 1 + z$
(iii) $1 - x, 0\cdot5 + y, 1 - z$

116 and 123° in ethyl carbamate (Bracher & Small, 1967) and 113·5 and 122·6° in Z-Gly-Pro (Tanaka *et al.*, 1977). This is a result of the interaction between the bulky *tert*-butyl group and the carbonyl group. These significant deformations of the bond angles around $C(4)$, $O(1)$ and $C(5)$ are common in several *tert*-Boc and *tert*-Aoc groups reported so far.

Crystal structure

The crystal structure is shown in Fig. 3, and the hydrogen bonds are listed in Table 4. The water molecule plays a role in forming the hydrogen-bond network. The $O(6)-H(O61)\cdots W(1)$ hydrogen bond of 2·598 Å is fairly short. The hydrogen bond between the non-ionized carboxyl group (donor) and the water molecule (acceptor) is usually strong (Ashida, Sasada & Kakudo, 1967).

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Fig. 3. Crystal structure. Hydrogen-bond lengths and $H\cdots$ acceptor distances (in parentheses) are shown.

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X-ray Structure of Two Analogues of the Carbohydrate Moiety of the Polyoxins

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The structures of two isomeric sugars, $C_{22}H_{29}NO_9$, have been studied by X-ray diffraction. Isomer (D) was shown to be ethyl 5-O-acetyl-3-O-benzyl-6-deoxy-6-formylamino-1,2-O-isopropylidene-D-*glycero*-L-*talo*-heptofuranuronate and crystallizes in the space group $P2_12_12_1$, with $a = 18\cdot40$ (1), $b = 14\cdot82$ (1), $c = 8\cdot65$ (1) Å, $Z = 4$. Isomer (C) was shown to be ethyl 5-O-acetyl-3-O-benzyl-6-deoxy-6-formylamino-1,2-O-isopropylidene-L-*glycero*-D-*allo*-heptofuranuronate and crystallizes in $P2_1$ with $a = 19\cdot50$ (1), $b = 8\cdot50$ (1), $c = 14\cdot99$ (1) Å, $\beta = 109\cdot0$ (1)°, $Z = 4$. The structures were refined to $R(D) = 0\cdot05$, $R(C) = 0\cdot07$. Packing forces cause the distortions which lead to the crystallographic dimerization.

Introduction

The discovery of the naturally occurring polyoxins (Suhadolnik, 1970) has led to interest in C—C linked sugar α-amino acids, and several compounds with C^α of an α-amino acid moiety attached to C(1), C(2), C(3) or C(4) of furanosyl sugars have been reported (Bischofberger, Brink, De Villiers, Hall & Jordaan, 1977, and references therein). Recently, similar compounds with an α-amino acid moiety attached to C(5)

of a furanosyl sugar have been prepared (Hall, Bischofberger, Brink, De Villiers & Jordaan, to be published) by reacting 3-O-benzyl-1,2-O-isopropylidene-α-D-*ribo*-pentodialdo-1,4-furanose with ethyl isocyanoacetate in ethanol in the presence of sodium cyanide. Hydrolysis of the two oxazoline derivatives obtained (Hoppe, 1974) gave two ethyl 3-O-benzyl-6-deoxy-6-formylamino-1,2-O-isopropylidene-heptofuranuronates [(A) and (B)] which were separated by column chromatography. Acetylation, with acetic