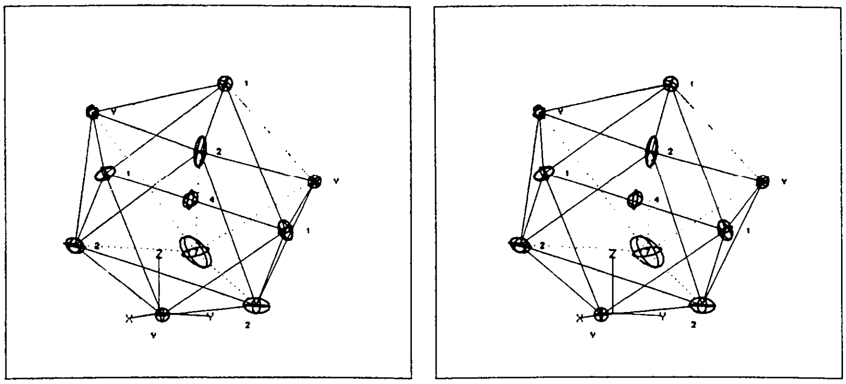

Fig. 5. Stereo drawing of the coordination about Cd(4). Details as in Figs. 2 and 3.

Table 3 (*cont.*)

Y–Cd(5)	3·614 (1)
Y–Cd(6)	3·365 (1)
Y–Cd(7)	3·801 (6)
Cd(1)–Y	3·256 (1)
Cd(1)–Y	3·353 (1)
Cd(1)–Y	3·341 (1)
Cd(1)–2Cd(1)	2·948 (1)
Cd(1)–Cd(2)	2·923 (1)
Cd(1)–Cd(3)	3·005 (1)
Cd(1)–Cd(3)	3·070 (1)
Cd(1)–Cd(4)	2·922 (1)
Cd(1)–Cd(5)	3·079 (1)
Cd(2)–Y	3·306 (1)
Cd(2)–2Y	3·393 (1)
Cd(2)–2Cd(1)	2·923 (1)
Cd(2)–Cd(2)	2·857 (2)
Cd(2)–2Cd(4)	2·975 (1)
Cd(2)–Cd(6)	2·924 (2)
Cd(2)–Cd(7)	2·583 (6)
Cd(4)–3Y	3·320 (7)
Cd(4)–3Cd(1)	2·922 (1)
Cd(4)–3Cd(2)	2·976 (1)
Cd(4)–Cd(7)	3·074 (3)
Cd(5)–4Cd(1)	3·079 (1)
Cd(5)–2Cd(3)	2·797 (1)
Cd(5)–2Cd(3)	2·831 (1)
Cd(5)–2Cd(6)	3·288 (1)
Cd(6)–2Y	3·365 (1)
Cd(6)–2Cd(2)	2·924 (2)
Cd(6)–4Cd(3)	3·165 (1)
Cd(6)–2Cd(5)	3·288 (1)
Cd(7)–Cd(7)	2·296 (12)
Cd(7)–Cd(7)	2·576 (10)
Cd(7)–2Cd(7)	2·985 (7)

We are indebted to V. O. Struebing for preparing the specimen.

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Refinement of the Crystal Structure of Tosyl-L-prolyl-L-hydroxyproline Monohydrate*

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The published X-ray diffraction data for tosyl-L-prolyl-L-hydroxyproline monohydrate have been refined by least-squares methods to an R index of 0·093. As a result, some structural parameters are markedly improved.

Introduction

This paper records briefly the refinement of the structure of tosyl-L-prolyl-L-hydroxyproline monohydrate (I) whose approximate structure was determined originally by Fridrichsons & Mathieson (1962). A straightforward refinement was thought desirable for two reasons: (*a*) interest in the accurate geometry and conformation of the proline ring, and (*b*) the nonplanarity of the peptide group in this structure. Fridrichsons & Mathieson stated that the peptide group is strictly

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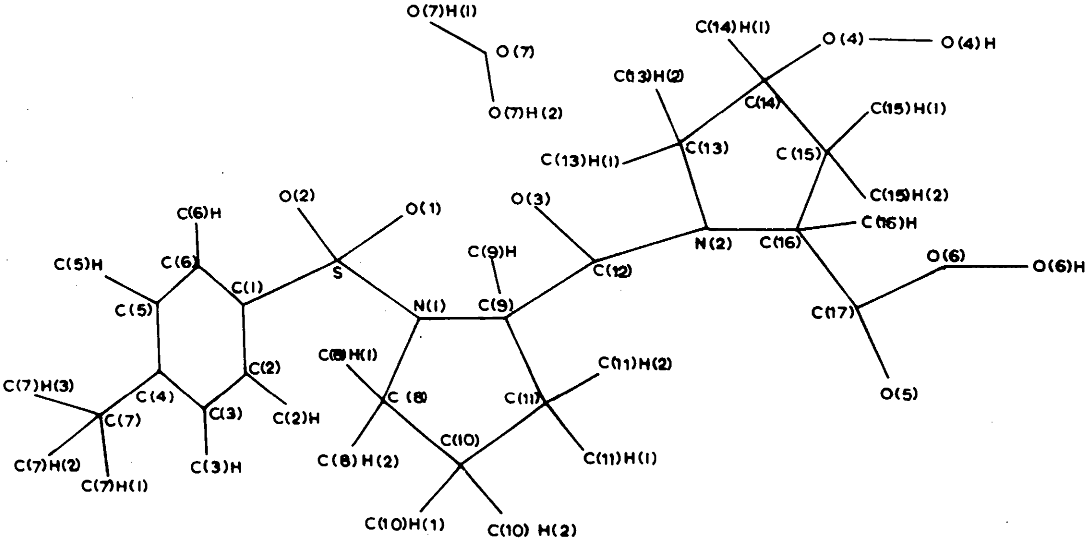
non-planar. But the peptide group is almost perpendicular to the *b* axis, and the nature of determining the positional coordinates attaches greater uncertainty to the *y* coordinates of the atoms. Therefore, the suspected non-planarity is of doubtful significance (Marsh & Donohue, 1967) in the absence of a complete refinement of the structure.



I

Refinement

The full-matrix least-squares refinement was carried out using the visually estimated data given in Table 2 of the paper by Fridrichsons & Mathieson (1962). The function minimized was $\sum W(|F_o|-k|F_c|)^2$. After two cycles of refinement employing unit weights, the *R* index dropped from 0·328 to 0·137. From a careful analysis of $\langle\Delta F^2\rangle/\sum\langle\Delta F^2\rangle$ *vs.* $|F_o|$, the weighting scheme $W=1/(a+|F_o|+b|F_o|^2)$, where $a=2{\cdot}12$ and $b=0{\cdot}04$, was chosen and all subsequent refinements were carried out with this scheme. Two further cycles of refinement decreased *R* to 0·128. At this stage, a difference Fourier synthesis was calculated which showed peaks near the regions where the hydrogen atoms were expected to occur. In this map, only reflexions for which $\sin\theta/\lambda\le$ 0·40 were used. All hydrogen atoms, except those attached to the water molecule and the one attached to O(4), appeared unambiguously in this map with heights varying from 0·20 to 0·35. e.Å^{-3}. In subsequent structure-factor calculations, the contribution from the hydrogen atoms was taken into account by assigning the isotropic temperature factor of the heavy atom to which they were bonded. No least-squares refinement of the positions, or the isotropic temperature factors, of the hydrogen atoms was attempted.

All refinements up to this stage were carried out on a CDC-3600 computer at Bombay using program *UCLALS* 1 written by Gantzel, Sparks & Trueblood (1961). Three more cycles of full-matrix least-squares refinement on an IBM-7094 computer at the University of Chicago, using a program written by Robert Dewar (modified version of program *ORFLS*; Busing, Martin & Levy, 1962,) was carried out treating all the non-hydrogen atoms anisotropically. All the reflexions were put on the same scale, and the overall scale factor was refined. As only about 170 parameters could be refined at a time with this program, the non-hydrogen atoms were divided into three blocks, out of which two blocks were refined per cycle. The final *R* index at the end of this refinement was 0·093.

Coordinates of all the non-hydrogen atoms at the end of the refinement, with their estimated standard

Table 1. *Coordinates (fractional) of non-hydrogen atoms and their e.s.d.'s in parentheses*

	x	*y*	*z*
S	1·1069 (4)	1·0000 (0)	0·1700 (1)
C(1)	0·9347 (15)	0·9728 (19)	0·0894 (5)
C(2)	1·0120 (19)	0·8923 (23)	0·0354 (6)
C(3)	0·8767 (20)	0·8883 (23)	−0·0301 (6)
C(4)	0·6740 (17)	0·9558 (19)	−0·0394 (5)
C(5)	0·6002 (16)	1·0375 (24)	0·0180 (6)
C(6)	0·7271 (16)	1·0384 (22)	0·0799 (5)
C(7)	0·5378 (24)	0·9546 (26)	−0·1106 (6)
C(8)	1·0664 (19)	0·6713 (19)	0·2169 (6)
C(9)	0·8446 (16)	0·8999 (19)	0·2563 (5)
C(10)	0·7538 (20)	0·7184 (22)	0·2669 (6)
C(11)	0·9311 (22)	0·5888 (29)	0·2673 (7)
C(12)	0·9050 (13)	0·9867 (18)	0·3264 (4)
C(13)	0·5347 (14)	1·1253 (17)	0·3106 (5)
C(14)	0·4500 (14)	1·2643 (17)	0·3512 (5)
C(15)	0·5613 (15)	1·2191 (19)	0·4256 (5)
C(16)	0·7882 (14)	1·1607 (15)	0·4165 (4)
C(17)	0·8691 (15)	1·0250 (21)	0·4694 (5)
N(1)	1·0374 (12)	0·8590 (16)	0·2255 (4)
N(2)	0·7513 (10)	1·0819 (13)	0·3472 (3)
O(1)	1·3180 (10)	0·9438 (15)	0·1597 (4)
O(2)	1·0676 (14)	1·1629 (14)	0·1952 (4)
O(3)	1·0810 (9)	0·9683 (13)	0·3630 (3)
O(4)	0·5186 (13)	1·4251 (13)	0·3280 (4)
O(5)	0·7908 (10)	0·8820 (13)	0·4685 (4)
O(6)	1·0263 (12)	1·0692 (14)	0·5200 (3)
O(7)	1·3978 (12)	0·7116 (16)	0·3990 (5)

deviations, are given in Table 1. Average differences between the coordinates obtained after the present refinement and the coordinates reported by Fridrichsons & Mathieson (1962) in x, y and z are 0·038, 0·163 and 0·043 Å respectively. The largest differences recorded are 0·154 Å in the x coordinate of C(8), 0·400 Å in the y coordinate of O(5) and 0·096 Å in the z coordinate of C(8). Anisotropic thermal parameters of all non-hydrogen atoms are listed in Table 2. Scattering factors of C, N, O and S atoms were taken from *International Tables for X-ray Crystallography* (1962). While the real part of the anomalous dispersion correction was taken into account for S ($\Delta f' = 0{\cdot}3$ for Cu $K\alpha$ radiation), the $\Delta f''$ correction could not be incorporated as the exact quadrants of the Weissenberg photographs in which the intensities were measured were not known.

Bond lengths and angles, calculated from the final coordinates of the non-hydrogen atoms, are listed in Table 3 with the corresponding values obtained by Fridrichsons & Mathieson (1962). The bond lengths and angles in the benzene ring are normal, with average values of 1·387 Å and 120·0° respectively. Variations in the bond distances in the benzene ring suggest that the real errors are somewhat higher than the formal e.s.d.'s. A detailed analysis of the bond length and angle distribution in the pyrrolidine ring, as observed in crystal structures containing prolyl and hydroxyprolyl residues, is presented elsewhere (Balasubramanian, Lakshminarayanan, Sabesan, Tegoni, Venkatesan & Ramachandran, 1970).

The mean S–O length of 1·413 Å agrees within experimental errors with the values found in other aromatic sulphonates, sulphonamides and related species (Meyers & Trueblood, 1969; O'Connell & Maslen, 1967; Hall & Maslen, 1965; Herdklotz & Sass, 1969). The carbon–sulphur distance of 1·777 Å agrees with the value expected of a C(sp^2)–S bond (Jacobs & Sundaralingam, 1969).

It has been well established that the C–S–O angles in sulphonate groups are always smaller than the tetrahedral angle, whereas the O–S–O angles are larger than the tetrahedral value (Okaya, 1967; Herdklotz & Sass, 1969). In the present structure, the same trend is observed with an average value of 107·0° for the C–S–O angles and 123·0° for the O–S–O angle.

Schomaker & Stevenson (1941) estimated the S–N single bond distance to be 1·74 Å; in sulphamic acid (which exists in the crystalline state as the zwitterion, the nitrogen atom having no orbitals available for π-bonding; Sass, 1960) the S–N length is 1·764 ± 0·020 Å. The S–N(1) distance (1·647 ± 0·009 Å) in the present structure is appreciably shorter, indicating a significant degree of double-bond character for this bond. Also, it is observed that the nitrogen coordination is close to planar; the sum of the three angles at N(1) is 351° and the deviation of the nitrogen atom N(1) from the plane through S, C(8) and C(9) is only 0·146 Å.

Distances within the peptide group are close to the expected values (Corey & Pauling, 1953; Marsh & Donohue, 1967). Although the angle C′–N–H in a peptide unit is presumed to be about 123°, in peptide groups containing proline at either the C-terminal or a central position, the C′–N–C angle is found to be somewhat larger: of average value 126·5° (Balasubra-

Table 2. *Anisotropic thermal parameters of all the non-hydrogen atoms* ($\times 10^4$) *and their e.s.d.'s in parentheses*

The b_{ij}'s are defined by: $\exp\,[-(h^2b_{11}+k^2b_{22}+l^2b_{33}+2hkb_{12}+2hlb_{13}+2klb_{23})]$.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S	307 (6)	242 (9)	29 (1)	−26 (6)	29 (1)	−4 (2)
C(1)	310 (24)	184 (31)	31 (2)	−14 (23)	34 (6)	−19 (8)
C(2)	394 (31)	282 (40)	31 (3)	20 (29)	38 (8)	−25 (9)
C(3)	459 (38)	300 (39)	29 (3)	37 (33)	19 (9)	−26 (9)
C(4)	422 (29)	197 (38)	28 (3)	−113 (26)	−3 (7)	15 (8)
C(5)	325 (24)	291 (49)	42 (4)	15 (28)	28 (7)	21 (11)
C(6)	365 (29)	286 (51)	36 (3)	91 (29)	44 (7)	15 (9)
C(7)	603 (46)	366 (53)	36 (3)	−102 (40)	−41 (10)	26 (11)
C(8)	418 (35)	108 (42)	35 (3)	45 (25)	34 (8)	1 (8)
C(9)	302 (24)	213 (35)	27 (2)	−49 (23)	24 (6)	−16 (7)
C(10)	440 (36)	184 (43)	42 (3)	−68 (30)	54 (9)	−17 (10)
C(11)	495 (41)	321 (48)	40 (4)	6 (39)	37 (11)	−10 (12)
C(12)	270 (20)	99 (25)	27 (2)	−7 (20)	24 (5)	−6 (7)
C(13)	268 (23)	107 (31)	28 (2)	17 (20)	5 (6)	−1 (6)
C(14)	276 (22)	129 (31)	29 (2)	−13 (20)	25 (6)	7 (7)
C(15)	270 (23)	230 (35)	31 (3)	26 (22)	20 (6)	8 (8)
C(16)	318 (24)	89 (28)	23 (2)	12 (19)	15 (6)	−2 (6)
C(17)	309 (25)	174 (39)	24 (2)	−58 (24)	10 (6)	−1 (7)
N(1)	296 (20)	156 (31)	29 (2)	12 (18)	23 (5)	−11 (6)
N(2)	239 (16)	155 (21)	23 (2)	31 (15)	14 (4)	1 (5)
O(1)	285 (17)	431 (34)	34 (2)	25 (18)	38 (5)	7 (6)
O(2)	560 (29)	120 (25)	38 (2)	−35 (20)	43 (7)	−9 (6)
O(3)	250 (14)	275 (23)	29 (2)	44 (16)	10 (4)	−1 (5)
O(4)	428 (23)	132 (23)	41 (2)	−3 (17)	28 (6)	−2 (6)
O(5)	319 (18)	193 (20)	33 (2)	−36 (16)	7 (5)	−3 (6)
O(6)	383 (20)	275 (26)	28 (2)	−23 (18)	−10 (5)	1 (5)
O(7)	370 (23)	271 (27)	47 (3)	43 (19)	10 (6)	−12 (7)

Table 3. *Bond lengths and angles with their e.s.d.'s*

Values reported by Fridrichsons & Mathieson (1962) are given in parentheses.

Lengths:		σ			σ
S——C(1)	1·777 (1·78) Å	0·011 Å	C(9)—C(12)	1·521 (1·51) Å	0·015 Å
S——N(1)	1·647 (1·60)	0·009	C(9)—N(1)	1·476 (1·49)	0·015
S——O(1)	1·442 (1·35)	0·009	C(10)–C(11)	1·495 (1·56)	0·022
S——O(2)	1·384 (1·38)	0·009	C(12)–N(2)	1·329 (1·32)	0·012
C(1)—C(2)	1·383 (1·38)	0·018	C(12)–O(3)	1·225 (1·24)	0·012
C(1)—C(6)	1·384 (1·38)	0·017	C(13)–C(14)	1·484 (1·54)	0·015
C(2)—C(3)	1·421 (1·40)	0·020	C(13)–N(2)	1·471 (1·43)	0·013
C(3)—C(4)	1·361 (1·41)	0·018	C(14)–C(15)	1·552 (1·54)	0·015
C(4)—C(5)	1·433 (1·37)	0·018	C(14)–O(4)	1·410 (1·45)	0·014
C(4)—C(7)	1·515 (1·54)	0·020	C(15)–C(16)	1·535 (1·53)	0·015
C(5)—C(6)	1·340 (1·43)	0·018	C(16)–C(17)	1·501 (1·52)	0·015
C(8)—C(11)	1·544 (1·56)	0·021	C(16)–N(2)	1·473 (1·45)	0·012
C(8)—N(1)	1·468 (1·50)	0·016	C(17)–O(5)	1·204 (1·19)	0·014
C(9)—C(10)	1·535 (1·56)	0·018	C(17)–O(6)	1·326 (1·41)	0·014
Angles:		σ			σ
C(1)—S——N(1)	108·8 (109·9)°	0·5°	C(8)—C(11)–C(10)	102·3 (95·1) °	1·5°
C(1)—S——O(1)	106·3 (105·8)	0·5	C(9)—C(12)–N(2)	115·7 (110·9)	1·1
C(1)—S——O(2)	107·8 (115·5)	0·5	C(9)—C(12)–O(3)	123·2 (132·7)	1·1
N(1)—S——O(1)	104·3 (118·6)	0·4	N(2)—C(12)–O(3)	121·1 (114·0)	1·1
N(1)—S——O(2)	106·1 (85·5)	0·4	C(14)–C(13)–N(2)	106·6 (98·3)	1·0
O(1)—S——O(2)	123·0 (120·7)	0·4	C(13)–C(14)–C(15)	101·4 (106·6)	1·0
S——C(1)—C(2)	119·7 (118·1)	1·0	C(13)–C(14)–O(4)	107·6 (108·5)	1·1
C(2)—C(1)—C(6)	120·2 (122·4)	1·3	C(15)–C(14)–O(4)	112·7 (109·3)	1·1
C(1)—C(2)—C(3)	118·0 (119·2)	1·4	C(14)–C(15)–C(16)	103·9 (103·0)	1·1
C(2)—C(3)—C(4)	121·4 (119·7)	1·5	C(15)–C(16)–C(17)	109·8 (114·7)	1·0
C(3)—C(4)—C(5)	118·6 (120·0)	1·3	C(15)–C(16)–N(2)	102·7 (103·7)	1·0
C(3)—C(4)—C(7)	119·8 (121·9)	1·3	C(17)–C(16)–N(2)	109·7 (117·6)	1·0
C(5)—C(4)—C(7)	121·4 (118·1)	1·2	C(16)–C(17)–O(5)	122·2 (123·4)	1·2
C(4)—C(5)—C(6)	119·6 (120·8)	1·4	C(16)–C(17)–O(6)	117·8 (112·0)	1·2
C(1)—C(6)—C(5)	121·9 (117·7)	1·3	O(5)—C(17)–O(6)	119·9 (124·7)	1·2
C(11)–C(8)—N(1)	103·8 (107·8)	1·3	S——N(1)—C(8)	121·3 (120·3)	0·8
C(10)–C(9)—C(12)	108·6 (100·7)	1·2	S——N(1)—C(9)	117·2 (115·6)	0·8
C(10)–C(9)—N(1)	102·2 (98·8)	1·2	C(8)—N(1)—C(9)	112·5 (111·6)	1·0
C(12)–C(9)—N(1)	111·4 (109·3)	1·1	C(12)–N(2)—C(13)	129·6 (125·4)	0·9
C(9)—C(10)–C(11)	108·2 (115·2)	1·3	C(12)–N(2)—C(16)	119·9 (114·8)	0·8
S——C(1)—C(6)	120·1 (119·3)	1·0	C(13)–N(2)—C(16)	110·5 (116·2)	0·8

manian, Lakshminarayanan, Sabesan, Tegoni, Venkatesan & Ramachandran, 1970). In the present structure this angle is 129·6 (0·9)°.

Although the aromatic ring is planar, attached atoms C(7) and S are displaced by 0·056 and 0·166 Å respectively (Table 4), and these deviations can be considered to be significant (4·5 σ for C(7) and 16 σ for S). Application of the χ^2 test to the displacements of the atoms of the peptide group C(9), C(12), O(3), N(2), C(16) and C(13) indicates that these atoms cannot all be regarded as coplanar ($\chi^2 = 50{\cdot}6$; Table 4). The deviation of the S atom from the plane of the benzene ring and the non-planarity of the peptide group are significant, even if the real standard deviations, as pointed out earlier, are assumed to be twice that of the formal e.s.d.'s. Note that the atoms C(9) and C(13) are displaced from the best plane passing through C(12), O(3), N(2) and C(16) by 0·100 and 0·046 Å respectively, and further that these two atoms lie on either side of this plane (Table 4). The internal rotation angle (ω) about the C(12)–N(2) bond(according to the definition proposed by Edsall, Flory, Kendrew, Liquori, Nemethy, Ramachandran & Scheraga, 1966) is $-4{\cdot}5°$. The deformation may be partly due to the intramolecular close approaches of C(13)$\cdots$C(9) (2·938 Å), C(17)$\cdots$O(3) (2·692 Å) and C(13)$\cdots$C(9)H (2·465 .Å) The small deformation of the peptide group may be significant in connection with the conformation of the polypeptide chains containing *cis* peptide units.

As observed in other crystal structures containing prolyl or hydroxyprolyl residues (Balasubramanian *et*

Table 4. *Least-squares planes*

Equation to the plane: $AX+BY+CZ=D$, with respect to the crystallographic axes a, b and c *, where X, Y, Z are in Å.

Atom	Deviation (Å)	Atom	Deviation (Å) Plane I	Plane II
S	0·166	C(9)	−0·045†	−0·102
C(1)	0·016†	C(12)	0·014†	−0·012†
C(2)	−0·008†	O(3)	0·034†	0·006†
C(3)	0·004†	N(2)	0·005†	0·010†
C(4)	−0·007	C(13)	0·032†	0·046
C(5)	0·014†	C(16)	−0·041†	−0·005†
C(6)	−0·019†			
C(7)	0·056			
A	0·410		0·425	0·413
B	0·880		0·811	0·825
C	−0·238		−0·402	−0·386
D	8·450		5·563	5·746
χ^2	6·5		50·6	3·2

† Atoms used for defining the plane.

Table 5. *Hydrogen bond lengths and angles*

The values given within parentheses are those reported by Fridrichsons & Mathieson (1962).

	Length (Å)		Angle (°)
O(7)···O(3)	2·811 (2·97)	C(12)–O(3)···O(7)	139·8 (126·2)
O(7)···O(5)	2·929 (2·81)	C(17)–O(5)···O(7)	136·7 (130·0)
O(7)···O(4)	2·780 (2·92)	C(14)–O(4)···O(7)	114·2 (117·0)
O(5)···O(6)	2·660 (2·49)	C(17)–O(6)···O(5)	123·7 (128·4)

al., 1970), the four atoms of the pyrrolidine ring are coplanar, while the fifth atom deviates from this plane. Deviations of atoms C(10) and C(15) from the planes formed by the other four atoms in the rings are 0·505 and 0·541 Å respectively. Although the isotropic temperature factor of the C^{γ} atom [C(10)] of the proline ring is larger than those of the other four atoms in the ring, the possibility of this atom being disordered was ruled out from a careful analysis of the difference map.

Hydrogen-bond distances and angles are listed in Table 5. Corresponding values obtained, using the positional coordinates of Fridrichsons & Mathieson (1962), are given in parentheses. The changes in all hydrogen-bond lengths after the present refinement are significant (Table 5). The water molecule is engaged in three O–H···O bonds. Two protons of the water molecule are involved in hydrogen bonds to O(3) and O(5) with lengths 2·811 and 2·929 Å respectively. The water molecule accepts a proton from the hydroxyl group O(4) of the hydroxyproline residue; the O(7)···O(4) length is 2·780 Å. Oxygen atom O(5) of the carboxyl group accepts a proton from O(6); the O(6)···O(5) distance is 2·659 Å. The displacement of the water molecule from the plane passing through atoms O(3), O(4) and O(5) is 0·55 Å.

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