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Note

Crystal structure of *N*-(1-deoxy-β-D-fructopyranos-1-yl)-L-proline—an Amadori compound

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Abstract—Here we report the crystal structure data on *N*-(1-deoxy-β-D-fructopyranos-1-yl)-L-proline (Fru-Pro)—an Amadori compound. X-ray crystal and molecular structures of its two isomorphous crystalline forms, (Fru-Pro)·MeOH, $C_{11}H_{19}NO_7{\cdot}CH_4O$ (**1a**) and (Fru-Pro)·$2H_2O$, $C_{11}H_{19}NO_7{\cdot}2H_2O$ (**1b**) were determined. In **1a** and **1b** the compound crystallizes as the β-anomer with the overall geometry of Fru-Pro zwitterions being very similar. Fructose ring adopts the chair $^2C_5$ conformation with the proline moiety bonded to equatorial C-1 atom and remaining in a *trans–gauche* (*tg*) orientation with respect to the sugar ring. The five-membered pyrrolidine ring adopts an envelope conformation, with the Cβ atom puckered. Fructosyl and carboxylate groups are in bisectional and axial positions of pyrrolidine ring, respectively. The overall molecular geometry of Fru-Pro zwitterions, especially the relative orientation of sugar and amino acid moieties, is stabilized by intramolecular, three-centred N–H···O_{Fru}/O_{Pro} hydrogen bonds (with bifurcated acceptor) formed between aminium and hydroxyl/carboxylate groups. The packing diagrams are very similar in both **1a** and **1b** with the adjacent zwitterions linked to each other by the extensive network of O–H···O and C–H···O hydrogen bonds to form channels along the *a*-axis, filled up with solvent molecules.

Keywords: Amadori compound; Fructosyl-proline; Fru-Pro; X-ray crystal structure

Amadori compounds are N-substituted (1-deoxy-ketos-1-yl)-amines representing an important class of relatively stable Maillard intermediates.[1] They are formed in the early stage of the Maillard reaction, called non-enzymatic browning,[2,3] by condensation of an amino acid with an aldose followed by Amadori rearrangement of the corresponding *N*-glycosylamine derivative.[4] The Amadori compounds play a significant role in the initial phase of the Maillard reaction—they can decompose and initiate a cascade of further reactions that finally result in formation of very complex mixtures.[5,6] These reactions take place during food processing and storage, as well as under physiological conditions, and may be involved in the pathology of diabetes and ageing. The Amadori compounds have been identified in naturally occurring materials such as fruit and vegetables.[7,8] They are also responsible for flavour and colour formation in processed foods. Additionally the Amadori compounds are present in peat extract (Tołpa® Peat Preparation)[9,10] and are responsible for its immunomodulatory effects. In this study the X-ray crystal and molecular structures of the *N*-(1-deoxy-β-D-fructopyranos-1-yl)-L-proline (Fru-Pro) were determined for its two crystalline forms: methanol monosolvate, (Fru-Pro)·MeOH, $C_{11}H_{19}NO_7{\cdot}CH_4O$ (**1a**) and dihydrate, (Fru-Pro)·$2H_2O$, $C_{11}H_{19}NO_7{\cdot}2H_2O$ (**1b**).

1-Deoxy-1-substituted fructose derivatives, especially sugar–amino acid compounds, have been poorly explored as regards their solid-state structures. The only X-ray data deposited so far with the Cambridge Structural Database[11] are five crystal structures: one of phosphate ester and four of N-substituted derivatives, viz.

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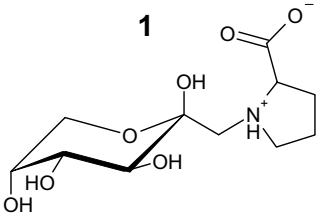
disodium β-D-fructopyranose 1-phosphate pentahydrate, $Na_2(Fru\text{-}OPO_3)\cdot 5H_2O$[12] [CSD refcode TARBIX], *N*-benzyl-*N*-methyl-(1-deoxy-β-D-fructopyranos-1-yl)-amine, Fru-N(Me)CH_2Ph[13] [CSD refcode BMAAHP10], *N*-(1-deoxy-β-D-fructopyranos-1-yl)-*p*-toluidine, Fru-NH(*p*Tol)[14] [CSD refcode ZIVTON], *N*,*N*-dibenzyl-(1-deoxy-β-D-fructopyranos-1-yl)-amine, Fru-$N(CH_2Ph)_2$[15] [CSD refcode UDEVUU] and *N*-(1-deoxy-β-D-fructopyranos-1-yl)-glycine, Fru-Gly[16] [CSD refcode YUXCUP]. Only the latter of these crystal structures is a sugar–amino acid compound. Very recently, another Amadori compound has been reported (Fru-L-His·H_2O).[17] Therefore we present the results of our single-crystal X-ray study of the title compound, Fru-Pro, in two crystalline forms: methanol monosolvate (**1a**) and dihydrate (**1b**), together with a comparison of the results with those previously reported for Fru-Gly, Fru-His and other Fru derivatives as well as fructose itself. The analysis of intermolecular interactions in the crystal network of **1a** and **1b** is also presented.

Molecular geometry of Fru-Pro zwitterions in **1a** *and* **1b** *crystals*

N-(1-Deoxy-β-D-fructopyranos-1-yl)-L-proline (Fru-Pro, **1**)



was formed in the Amadori rearrangement of D-glucose and L-proline. The compound was obtained in two crystalline forms, as methanol monosolvate, (Fru-Pro)·MeOH, $C_{11}H_{19}NO_7\cdot CH_4O$ (**1a**) and dihydrate, (Fru-Pro)·$2H_2O$, $C_{11}H_{19}NO_7\cdot 2H_2O$ (**1b**). In both crystals the compound is shown to crystallize as the β-anomer, which is the only anomeric form so far observed in all the crystal structures of fructopyranose and its simple complexes, with the coordinates deposited with the CSD.[11] In **1a** and **1b** crystal forms, Fru-Pro is present as a zwitterion (analogous to that observed in Fru-Gly and Fru-His·H_2O crystals) with the carboxylic group deprotonated and the pyrrolidine ring N atom protonated. Structures **1a** and **1b** crystallize in the same space groups and are isomorphous. Both methanol in **1a** and water molecules in **1b** are disordered into two positions (see Section 1). The molecular geometry of *N*-(1-deoxy-β-D-fructopyranos-1-yl)-L-proline zwitterion is very similar in both **1a** and **1b** (Fig. 1). The pyranosyl carbohydrate moiety adopts the chair $^2C_5$ conformation with Cremer and Pople[18] puckering parameters for **1a** and **1b** given in Table 1. It should be noted that the chair $^2C_5$ is the only conformation observed in the known

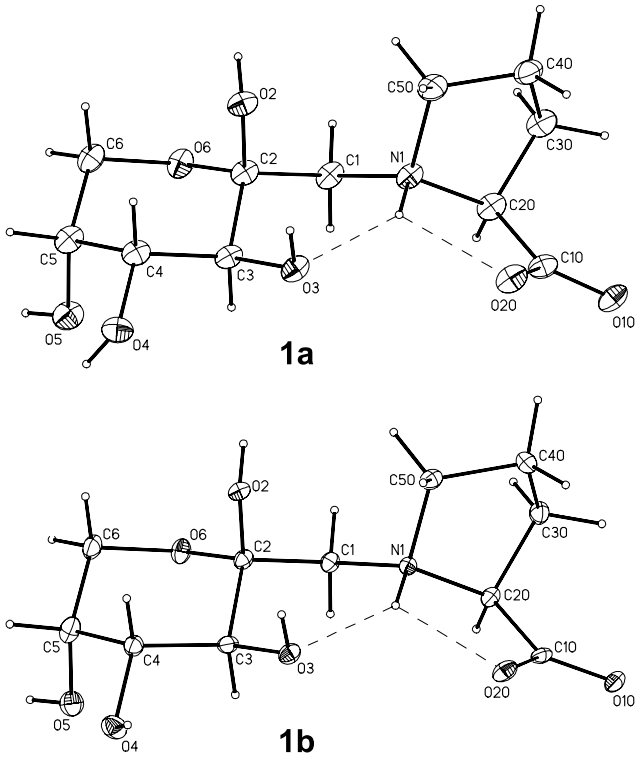


Figure 1. The molecular structures of *N*-(1-deoxy-β-D-fructopyranos-1-yl)-L-proline zwitterions in **1a** and **1b** showing the atom numbering scheme and the intramolecular bifurcated N1–H1···O3 and N1–H1···O20 hydrogen bonds forming *S*(6) and *S*(5) motifs, respectively (dashed line). Displacement ellipsoids are shown at the 30% probability level.

Table 1. Cremer and Pople[18] puckering parameters for fructopyranose ring and pseudorotation parameters[19] *P* and τ_m for proline (reference bond N1–C20) in **1a** and **1b**

	1a	**1b**	
Fructose ring			
Q (Å)	0.579(4)	0.567(4)	$^2C_5$
Θ (°)	178.8(4)	178.9(4)	
Φ (°)	294(12)	171(14)	
Proline ring			
P (°)	237.6(3)	233.5(3)	*E* (Cβ puckered)
τ_m (°)	43.5(3)	44.9(2)	

solid-state structures of fructopyranose and its complexes.[1111]

The exocyclic, anomeric C2–O2 distances in both **1a** and **1b** are significantly shorter (see the relevant values in Table 2), which was previously observed for β-D-fructose itself and β-D-fructose moieties in its derivatives: hydrated calcium chloride, calcium bromide and strontium chloride complexes and 1-substituted β-D-fructopyranose derivatives such as $Na_2(Fru\text{-}OPO_3)\cdot 5H_2O$[12] [CSD refcode TARBIX], Fru-N(Me)CH_2Ph[13] [CSD refcode BMAAHP10], Fru-$N(CH_2Ph)_2$[15] [CSD refcode UDEVUU] and Fru-Gly[16] [CSD refcode YUXCUP]. In both **1a** and **1b**, the anomeric shortening is accompanied by a slight shortening of the adjacent ring C2–O6

Table 2. Selected interatomic distances (Å), valence angles (°) and torsion angles (°) in **1a** and **1b** (standard deviations in parentheses)

	1a	**1b**		**1a**	**1b**
Bond lengths					
O2–C2	1.402(4)	1.398(4)	N1–C1	1.502(5)	1.501(4)
O3–C3	1.421(4)	1.419(4)	C1–C2	1.530(5)	1.528(5)
O4–C4	1.433(5)	1.431(4)	C2–C3	1.538(5)	1.557(5)
O5–C5	1.431(5)	1.449(5)	O10–C10	1.261(5)	1.249(4)
O6–C2	1.422(4)	1.412(4)	O20–C10	1.257(5)	1.258(5)
O6–C6	1.462(5)	1.443(4)			
Valence angles					
C2–O6–C6	113.3(3)	113.8(3)	O6–C2–C3	110.4(3)	110.3(3)
O2–C2–O6	112.4(3)	112.4(3)	C1–C2–C3	112.7(3)	111.6(3)
O2–C2–C1	112.5(3)	113.0(3)	O10–C10–O20	126.8(4)	127.1(3)
O6–C2–C1	102.4(3)	103.2(3)	O10–C10–C20	116.0(3)	116.8(3)
O2–C2–C3	106.6(3)	106.4(3)	O20–C10–C20	117.2(3)	116.1(3)
Endocyclic torsion angles					
C6–O6–C2–C3	60.4(4)	60.7(4)	C50–N1–C20–C30	−23.3(4)	−26.9(4)
O6–C2–C3–C4	−57.7(4)	−55.0(4)	C20–N1–C50–C40	−2.9(4)	0.4(4)
C2–C3–C4–C5	56.1(4)	52.2(4)	N1–C20–C30–C40	40.4(4)	42.8(4)
C3–C4–C5–C6	−55.8(4)	−53.9(4)	C20–C30–C40–C50	−42.0(4)	−42.5(4)
C2–O6–C6–C5	−59.1(4)	−61.2(4)	C30–C40–C50–N1	27.8(4)	26.2(4)
C4–C5–C6–O6	55.3(4)	56.2(4)			
Other torsion angles					
C6–O6–C2–O2	−58.4(4)	−57.9(4)	O4–C4–C5–O5	−57.1(4)	−54.2(4)
C6–O6–C2–C1	−179.3(3)	−179.9(3)	C3–C4–C5–O5	66.6(4)	68.0(4)
N1–C1–C2–O2	53.5(4)	55.2(4)	O4–C4–C5–C6	−179.5(3)	−176.2(3)
N1–C1–C2–O6	174.4(3)	176.8(3)	O5–C5–C6–O6	−65.0(4)	−64.7(4)
N1–C1–C2–C3	−67.0(4)	−64.7(4)	C2–C1–N1–C20	162.0(3)	161.8(3)
O2–C2–C3–O3	−60.5(4)	−57.2(4)	C2–C1–N1–C50	−76.5(4)	−76.3(4)
O6–C2–C3–O3	177.3(3)	−179.5(3)	C1–N1–C20–C30	102.8(4)	99.3(3)
C1–C2–C3–O3	63.4(4)	66.4(4)	C1–N1–C20–C10	−138.8(3)	−141.7(3)
O2–C2–C3–C4	64.6(4)	67.2(4)	C50–N1–C20–C10	95.1(4)	92.1(3)
C1–C2–C3–C4	−171.5(3)	−169.1(3)	O10–C10–C20–N1	179.2(3)	−174.9(3)
O3–C3–C4–O4	−56.5(4)	−62.3(4)	O10–C10–C20–C30	−66.7(4)	−61.5(4)
C2–C3–C4–O4	180.0(3)	173.7(3)	C10–C20–C30–C40	−76.2(4)	−73.7(4)
O3–C3–C4–C5	179.5(3)	176.2(3)	C1–N1–C50–C40	−128.6(3)	−125.6(3)

bonds with respect to C6–O6 distance being significantly longer. That was observed earlier, also in Fru-Gly and Fru-His·H_2O, but not in Na_2(Fru-OPO_3)·5H_2O, Fru-N(Me)CH_2Ph and Fru-N(CH_2Ph)$_2$.

The proline moiety is bonded to the equatorial fructosyl C1 atom and remains in a *trans–gauche* (*tg*) orientation with respect to the sugar ring (distorted by only about 5° from a staggered conformation; see the relevant N1–C1–C2–O6 and N1–C1–C2–C3 torsion angles in Table 2). It should be noted here that the conformation of the fructosyl free C1–O1 hydroxymethyl group is usually shown to be *gauche–gauche* (*gg*), rarely *gauche–trans* (*gt*), which was observed only in dihydrated Fru·$CaCl_2$ and Fru·$CaBr_2$ complexes. In 1-substituted β-D-fructopyranose derivatives, the oxygen or nitrogen atom is *gauche–gauche* orientated in Na_2(Fru-OPO_3)·5H_2O and Fru-NH(*p*Tol), or *gauche–trans*—in Fru-N(Me)-CH_2Ph, Fru-N(CH_2Ph)$_2$ and in Fru-His·H_2O. The only compound with a *trans–gauche* conformation of CH_2–X bond, of those so far investigated in solid-state, is the fructose–amino acid compound, Fru-Gly.[16] It has to be stressed that such *trans–gauche* (*tg*) conformation is rarely observed in pyranose carbohydrate structures.[11]

The five-membered pyrrolidine ring in **1a** and **1b** adopts an envelope conformation, with the Cβ atom (C30) lying out of the ring plane; the dihedral angles between the N1/C20/C40/C50 and C20/C30/C40 planes are 41.8(3)° in **1a** and 43.3(3)° in **1b**. It has to be noted that Cβ-puckered envelope conformation of the pyrrolidine ring has never been observed for any N-substituted proline derivatives so far deposited with the CSD.[11] The puckering usually found in compounds of this type are various twisted conformations (*T* on Cγ–Cδ, N–Cα or N–Cδ) or envelope puckered on Cγ or Cδ.

The pyrrolidine ring substituents, that is, fructosyl and carboxylate groups, are in bisectional and axial positions, respectively. The angles between the relevant N1–C1 and C20–C10 bonds and normal to N1/C20/C40/C50 Cremer and Pople plane are 35.4(3)° and 10.5(3)° for **1a** and 33.1(2)° and 8.5(2)° for **1b**. One of the carboxylate oxygen atoms, O10, is in antiperiplanar (*ap*) orientation relative to the pyrrolidine N atom, with

the other, O20, being synperiplanar (*sp*) (see the O10–C10–C20–N1 torsion angles values close to 180° in Table 2 for **1a** and **1b**), which is rather characteristic of this class of compounds.

Such a conformation in both crystal forms is stabilized by intramolecular N1–H1···O20 hydrogen interaction formed between aminium and carboxylate groups. Additionally, N1 acts as a donor of the other N1–H1···O3 intramolecular hydrogen bond to fructose hydroxyl atom O3 (see Fig. 1). This results in three-centred (with bifurcated acceptor) N1–H1···O3/O20 hydrogen bonds forming *S*(6) and *S*(5) motifs, respectively (shown in Fig. 1 with dashed lines), which stabilizes the overall molecular geometry, especially the relative orientation of sugar and amino acid moieties.

Crystal packing and intermolecular interactions in **1a** *and* **1b** *crystals*

In addition to intramolecular N–H···O interactions described above, the crystal structures of **1a** and **1b** are stabilized by the network of intermolecular Fru-Pro···Fru-Pro hydrogen contacts of O–H···O type, in which all the fructose hydroxyl groups act as donors and proline O10 and O20 atoms, along with the fructose hydroxyl O4 and O5 atoms functioning as acceptors. The packing diagrams are very similar in both **1a** and **1b**. The adjacent zwitterions are linked by a rather extensive network of O–H···O hydrogen bonds, several of which are almost identical in **1a** and **1b** (see Table 3 and Figs. 2 and 3). Hydroxyl O2 and O3 groups from fructose moiety of one zwitterion interact with carboxylate $O20^{i}$ and $O10^{ii}$ atoms from proline parts of two adjacent, symmetry related zwitterions. In addition, O5 hydroxyl group from the same zwitterion is involved in contact to hydroxyl $O4^{iv}$ oxygen atom from another (symmetry codes are listed in Table 3). The geometry of these interactions (along with most of C–H···O contacts) is almost identical in both **1a** and **1b** (see Table 3). Fructose hydroxyl O4 group forms different contacts in the two crystalline forms of Fru-Pro: to $O5^{iii}$ hydroxyl atom from adjacent zwitterion in **1a** and to O1W water molecule in **1b**. Nevertheless, all these intermolecular Fru-Pro···Fru-Pro interactions result in channels formed along the *a*-axis in the crystal structures of both **1a** and **1b** (see Fig. 3).

It seems probable that the role of solvent molecules (methanol in **1a** and two water molecules in **1b**) is less crucial for the crystal packing of **1a** and **1b**. Both methanol and water molecules are involved in hydrogen bonds network building, mainly as donors of O–H···O interactions, but also as acceptors (like both water molecules in **1b**). However, the solvent is located in the channels built up from Fru-Pro zwitterions, which may be the reason for the disorder of MeOH and water molecules observed in the crystals of **1a** and **1b**, respectively (see Section 1).

Table 3. Geometry of proposed hydrogen bonds and close C–H···O contacts for **1a** and **1b** (Å, °)

D–H···A	H···A (Å)	D···A (Å)	D–H···A (°)
Fru-Pro·MeOH (**1a**)			
O2–H2O···$O20^{i}$	1.84	2.676(4)	175
O3–H3O···$O10^{ii}$	1.93	2.747(4)	165
O4–H4O···O5	2.36	2.798(4)	113
O4–H4O···$O5^{iii}$	2.40	2.818(4)	111
O5–H5O···$O4^{iv}$	1.99	2.818(4)	168
N1–H1···O3	2.06	2.830(4)	139
N1–H1···O20	2.09	2.609(4)	114
O1M–H1M···$O10^{ii}$	1.91	2.749(5)	176
C1–H1A···$O20^{v}$	2.69	3.521(5)	142
C1–H1B···$O2^{vi}$	2.66	3.317(5)	124
C1–H1B···$O10^{i}$	2.45	3.368(5)	154
C4–H4···O1M	2.58	3.136(5)	115
C5–H5···$O5^{iv}$	2.48	3.179(5)	126
C20–H20···$O20^{v}$	2.41	3.398(5)	169
C50–H50A···$O10^{i}$	2.62	3.502(5)	148
C50–H50B···$O6^{vii}$	2.46	3.143(5)	126
Fru-Pro·2H$_2$O (**1b**)			
O2–H2O···$O20^{i}$	1.86	2.694(4)	174
O3–H3O···$O10^{ii}$	1.92	2.746(4)	165
O4–H40···O1W	1.92	2.736(8)	163
O5–H5O···$O4^{iv}$	1.93	2.764(4)	172
N1–H1···O3	2.06	2.837(4)	140
N1–H1···O20	2.08	2.598(4)	114
O1W–H1W···O2W	2.11	2.961(14)	166
O2W–H3W···$O10^{ii}$	2.12	2.893(6)	148
O2W–H4W···$O5^{viii}$	2.25	2.793(6)	120
C1–H1A···$O20^{v}$	2.55	3.390(5)	142
C1–H1B···$O2^{vi}$	2.68	3.337(5)	124
C1–H1B···$O10^{i}$	2.55	3.483(4)	156
C5–H5···$O5^{iv}$	2.60	3.266(5)	124
C5–H5···$O2W^{ix}$	2.60	3.591(7)	169
C20–H20···$O3^{v}$	2.70	3.191(5)	111
C20–H20···$O20^{v}$	2.34	3.311(5)	165
C30–H30A···$O2^{vi}$	2.69	3.525(5)	142
C40–H40A···$O2W^{v}$	2.63	3.482(8)	144
C50–H50A···O2	2.58	2.948(4)	102
C50–H50A···$O10^{i}$	2.71	3.552(5)	143
C50–H50B···$O6^{vii}$	2.48	3.005(5)	113

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, y-1/2, -z+3/2$; (iii) $x+1/2, -y+3/2, -z+1$; (iv) $x-1/2, -y+3/2, -z+1$; (*v*) $-x+1, y+1/2, -z+3/2$; (vi) $-x, y+1/2, -z+3/2$; (vii) $-x, y-1/2, -z+3/2$; (viii) $x, y-1, z$; (ix) $x-1/2, -y+1/2, -z+1$.

The crystal structures of two crystalline forms of the title compound are additionally stabilized by the extensive network of C–H···O hydrogen interactions. Geometry of proposed hydrogen bonds and close contacts for **1a** and **1b** is given in Table 3.

1. Experimental

1.1. General methods

All reagents and solvents were purchased in high commercial quality and were used without further purification.

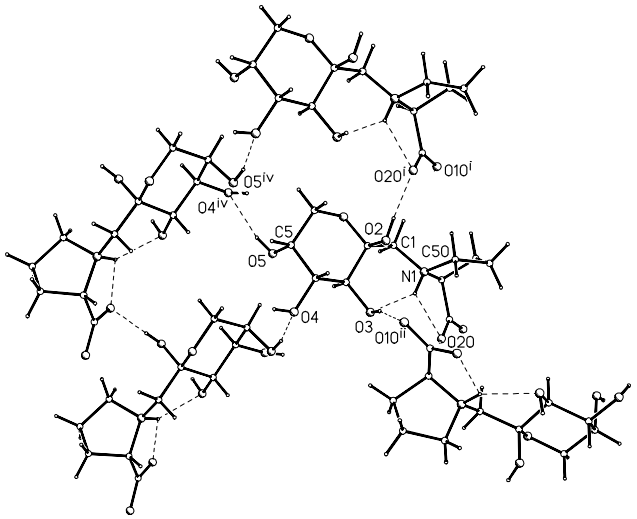


Figure 2. The intermolecular Fru-Pro···Fru-Pro hydrogen contacts of O–H···O type (dashed lines) in **1a**. The same contacts are also present in the crystal of **1b**. Intramolecular N–H···O bonds are also shown with dashed lines. Symmetry codes are listed in Table 3.

1.2. Synthesis of *N*-(1-deoxy-β-D-fructopyranos-1-yl)-L-proline

N-(1-Deoxy-β-D-fructopyranos-1-yl)-L-proline was prepared using general methods, similarly as previously described.[20] The resulting solid was suspended in MeOH and filtered off, washed with MeOH, finally recrystallized from hot MeOH and vacuum dried. The product (yield 40%) was min. 98% pure according to HPLC analysis. The identity of the product was confirmed using ESIMS and elemental analysis and these data were in agreement with lit.[7]

1.3. Crystal structure determination

Colourless crystals of **1a** suitable for single-crystal X-ray diffraction experiment were obtained by dissolving the material in MeOH and allowing the slow evaporation of the solvent at room temperature. Crystals of **1b** were grown from water solution of the compound, concentrated to thin syrup and seeded by crystals of **1a**.

The crystallographic measurements were performed on κ-geometry *Xcalibur PX* and Kuma *KM4CCD* automated four-circle diffractometers with graphite–monochromatized CuK_α and MoK_α radiation for **1a** and **1b**, respectively. The data for the crystals were collected at 100(2) K using the *Oxford Cryosystems* cooler. A summary of the conditions for the data collection and the structure refinement parameters are given in Table 4. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data collection, cell refinement and data reduction and analysis were carried out with the *Xcalibur PX* or *KM4CCD* software (*Oxford Diffraction Poland*): *CrysAlis CCD* and *CrysAlis RED*, respectively.[21] The structures were solved by direct methods using the SHELXS-97 program[22] and refined by a full-matrix least-squares technique using SHELXL-97[23] with anisotropic thermal parameters for ordered and high occupied non-H atoms. Most of the H atoms were found in difference Fourier maps. In the final refinement cycles, all the H atoms (except for those from water molecules in **1b**) were treated as riding atoms, with O–H distances of 0.84 Å, N–H distances of 0.93 Å and C–H distances of 0.98–1.00 Å, and with U_{iso} values of $1.5U_{eq}$(O,C) for OH and CH_3 groups, and $1.2U_{eq}$(O,N,C) for H_2O, NH, CH_2 and CH groups.

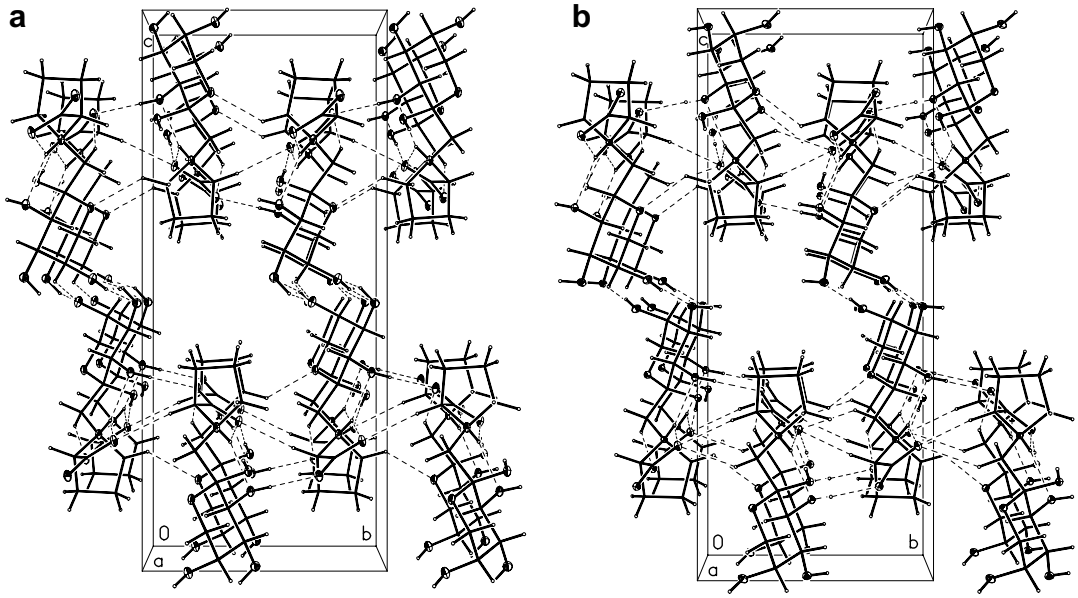


Figure 3. The arrangement of Fru-Pro zwitterions in the crystal of **1a** (a) and **1b** (b) showing the similarities in the crystal packing modes of two crystalline forms; viewed down the *a*-axis. Channels formed along the *a*-axis are filled up with solvent molecules, which are here omitted for clarity.

Table 4. Crystal data and structure refinement details for **1a** and **1b**

	(Fru-Pro)·MeOH (**1a**)	(Fru-Pro)·2H_2O (**1b**)
Crystal data		
Empirical formula	$C_{12}H_{23}NO_8$	$C_{11}H_{23}NO_9$
Moiety formula	$C_{11}H_{19}NO_7{\cdot}CH_4O$	$C_{11}H_{19}NO_7{\cdot}2H_2O$
Formula weight (g mol^{-1})	309.31	313.30
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.865(2)	6.815(3)
b (Å)	9.516(3)	9.212(4)
c (Å)	21.940(10)	22.422(8)
V (Å^3)	1433.3(9)	1407.6(10)
Z	4	4
D_{calc} (g cm^{-3})	1.433	1.478
μ (mm^{-1})	1.032	0.129
$F(000)$	664	672
Crystal size (mm)	$0.35\times0.25\times0.04$	$0.50\times0.25\times0.10$
Crystal colour and form	Colourless plate	Colourless plate
Data collection		
Diffractometer	Xcalibur PX	Kuma KM4CCD
Data collection method	ω Scans and φ scans	ω Scans
Monochromator	Graphite	Graphite
Radiation type	CuK_α	MoK_α
Wavelength, λ (Å)	1.5418	0.71073
T (K)	100(2)	100(2)
θ Range (°)	4.03–76.73	3.12–27.99
Indexes range	$-8\leqslant h\leqslant 4$, $-11\leqslant k\leqslant 11$, $-27\leqslant l\leqslant 23$	$-7\leqslant h\leqslant 9$, $-11\leqslant k\leqslant 11$, $-29\leqslant l\leqslant 28$
Measured reflections	10927	11533
Independent reflections	1711	1935
Observed reflections ($I>2\sigma(I)$)	1449	1758
R_{int}	0.0469	0.0611
Refinement		
Refinement on	F^2	F^2
Data/restraints/parameters	1711/0/204	1935/10/222
R ($F_o^2>2\sigma(F_o^2)$)	$R_1=0.0524$; $wR_2=0.1331$	$R_1=0.0574$; $wR_2=0.1344$
R (all data)	$R_1=0.0621$; $wR_2=0.1379$	$R_1=0.0650$; $wR_2=0.1376$
GooF = S	1.047	1.138
Weighting parameter a/b	0.0804/0.8740	0.0501/1.8409
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.30/−0.38	0.37/− 0.47

$R_1=\sum\|F_o|-|F_c\|/\sum|F_o|$; $wR_2=\sqrt{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]}$; weighting scheme: $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$.

Friedel opposites for both **1a** and **1b** crystals were merged and the absolute configuration was established on the basis of the known stereochemistry. For both crystals the extinction was also refined with the final extinction coefficients amounting to 0.0035(8) and 0.007(3) for **1a** and **1b**, respectively. All figures were made with XP program.[24] Cremer and Pople puckering parameters as well as pseudorotation parameters were calculated using PLATON program.[25]

Both MeOH in **1a** and water molecules in **1b** are disordered into two positions denoted as O1M–C1M (s.o.f. = 0.864(9)), O10M–C10M (s.o.f. = 0.136(9)) for MeOH in **1a** and O1W (s.o.f. = 0.82(4)), O10W (s.o.f. = 0.18(4)) and O2W (s.o.f. = 0.654(15)), O20W (s.o.f. = 0.346(15)) for two water molecules in **1b**. The positions of disordered solvent molecules with low site-occupation-factors were not taken into account in the discussion. Water H atoms in **1b** are fully occupied (shared by two disordered O atom positions) and were found in difference Fourier maps and refined with $U_{iso}=1.2U_{eq}(O)$ Å and with the O–H distances constrained to 0.86 Å. MeOH carbon atoms in **1a**, C1M and C10M, were refined with the same x, y, z coordinates and anisotropic displacement parameters (constraints were applied with EXYZ and EADP instructions).

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Supplementary data

Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallo-

graphic Data Centre, CCDC No. 628806 for **1a** and 628807 for **1b**. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2007.03.007.

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