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Single Crystals of V-Amylose Complexed with Bicyclic Organic Compounds

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Abstract

Lamellar single crystals of V-amylose were prepared from dilute aqueous solutions in the presence of selected bicyclic compounds. Transmission electron microscopy images as well as electron and X-ray diffraction patterns revealed that two allomorphs containing 7-fold amylose single helices were formed depending on the complexing agent. On the one hand, *trans*-decalin and (-)- β -pinene induced the crystallization of an orthorhombic unit cell isomorphous to that of V_{2-propanol} crystals reported in the literature (referred to as V7_{II}). On the other hand, (+)-camphor and (-)-borneol yielded a new compact pseudo-hexagonal structure (referred to as V7_I). *Cis*-decahydro-1-naphthol and decahydro-2-naphthol induced the formation of both allomorphs. V7_I was favored at a higher crystallization temperature compared to V7_{II}. Upon drying in vacuum, both V7_I and V7_{II} converted into the hexagonal anhydrous allomorph V7_a but the initial structures were recovered by rewetting the crystals in water at room temperature. In addition, washing the crystals with methanol resulted in a transition from a 7-fold to a 6-fold helical conformation of amylose. The results suggest that both water and complexing agent play an important role on the formation and stability of V-amylose crystals.

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1. Introduction

Amylose, the mostly linear constituent of native starch composed of $\alpha(1,4)$ -linked glucosyl units with less than 1% $\alpha(1,6)$ branching points, can form crystallosolvates with a large variety of small organic molecules such as fatty acids, alcohols, aldehydes, ketones or esters.^[1-3] When crystallized from dilute aqueous solutions, the so-called "V-amylose" complexes occur in the form of lamellar crystals involving chain folding. The amylose single helices are oriented perpendicular to the lamellae with a thickness, or folding length, of about 10 nm.^[4-6] The guest complexing agent is thought to be located inside the amylose helices, in-between, or both.^[7]

Different types of V-amylose have been characterized and described in the literature. They can be classified into families based on the number of glucosyl units per helix turn (6, 7 or 8) and the space available between the amylose helices in the unit cell.^[8,9] V_{6I} (also called V_h), prepared for instance with ethanol or fatty acids,^[10-11] V_{6II}, prepared with *n*-butanol,^[12] and V_{6III}, prepared with glycerol,^[13] contain 6-fold helices. The previously proposed occurrence of 7-fold helices (V₇ structure)^[4] has recently been demonstrated for complexes with 2-propanol.^[7,14] Finally, a V₈ structure has been reported for complexes with 1-naphthol^[8,15,16] and quinoline.^[8,15]

The role of the complexing agent in the determination of the helical conformation of V-amylose has been the subject of many investigations.^[8,17-20] A number of results suggest that linear compounds with a cross-sectional diameter of about 0.30 nm, *e.g.* fatty acids and *n*-alcohols, induce the formation of 6-fold amylose helices, while branched and cyclic compounds which a cross-sectional diameter is about 0.45-0.60 nm promote the formation of 7-fold helices. Amylose adopts an 8-fold conformation in the presence of a few bulkier bicyclic complexing agents such as 1-naphthol and quinoline.^[8,15,16]

However, some authors have reported that some complexing agents such as fatty acids,^[21,22] 2-propanol and quinoline^[8] could induce more than one amylose conformation, depending on the crystallization conditions (temperature, concentration of complexing agent, nature of the solvent). In addition, Helbert^[8] mentioned that some bicyclic compounds like quinoline, *trans*-decalin and (-)-borneol induced the formation of the V_{6I} allomorph, although their molecular dimension was not compatible with the inner cavity of a 6-fold helix. However, neither images nor diffraction patterns of these complexes were provided to support this observation.

Since the size of bicyclic compounds seems to be compatible with the cavity of both 7- and 8-fold helices, we have investigated the crystallization of amylose in the presence of a selection of such bicyclic compounds from dilute aqueous solutions, at different temperatures. The

morphology and structure of the resulting lamellar crystals were studied using transmission electron microscopy (TEM) as well as electron and X-ray diffraction (ED, XRD, respectively).

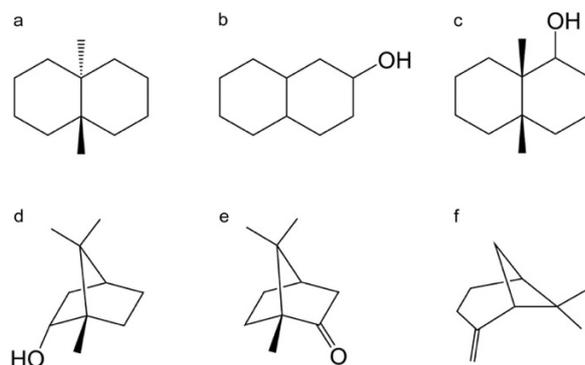


Figure 1. Chemical structure of the tested bicyclic complexing agents: a) *trans*-decalin, b) decahydro-2-naphthol, c) *cis*-decahydro-2-naphthol, d) (-)-borneol, e) (+)-camphor, f) (-)-β-pinene.

2. Experimental section

2.1. Amylose and bicyclic organic compounds

Potato amylose (number-average degree of polymerization DP_n 2500) was purchased from Sigma-Aldrich and further purified as previously described.^[22] *Trans*-decahydronaphthalene (*trans*-decalin - TDEC), (-)-β-pinene (BPIN), decahydro-2-naphthol (DNAP), *cis*-decahydro-1-naphthol (CDNAP), (-)-borneol (BORN) and (+)-camphor (CAMP) were purchased from Sigma-Aldrich and used as-received. The molecular structure of these complexing agents is shown in **Figure 1**. TDEC, BPIN, and DNAP are liquids at room temperature, while CDNAP, BORN and CAMP are solids. All these molecules have a very low solubility in water at room temperature.

2.2. Crystallization protocols

Amylose (10 mg) and an excess amount of complexing agent (15 mg for solid agents and 0.1 mL for liquid ones) were dispersed in 10 mL water, submitted to nitrogen bubbling during 20 min, autoclaved in an oil bath at 160 °C for 30 min and incubated at different temperatures (25, 40, 50, 60, 75, 100 and 115 °C). After one week, the solid precipitates were recovered by decantation then centrifugation (3600 g, 15 min), and washed three times at room temperature in water saturated with the complexing agent. In the case of CDNAP and DNAP, a recrystallization step was carried out to obtain more individualized lamellar crystals. The crystal suspensions were heated up to about 90 °C to redissolve the crystals, then cooled back to the crystallization temperature to allow the complexes to reform.

2.3. *Drying and rehydration*

The crystals were thoroughly dried in vacuum for several days. One part of the crystals was kept under vacuum, while the other part was redispersed in water and kept at room temperature for one day.

2.4. *Treatment of the crystals with methanol*

The crystals were washed three times by successive centrifugations in methanol at room temperature. Part of these crystals was stored as a suspension in methanol. The other part was dried under vacuum.

2.5. *X-ray diffraction (XRD)*

The crystal suspensions in water or in methanol were centrifuged and the pellets were deposited on absorbent paper for a few minutes to remove the excess of solvent. These samples as well as vacuum-dried ones were introduced into 1 mm (outer diameter) glass capillaries that were immediately flame-sealed and X-rayed in vacuum with a Ni-filtered CuK α radiation ($\lambda = 0.1542$ nm) using a Philips PW3830 generator operating at 30 kV and 20 mA. Two-dimensional diagrams were recorded on Fujifilm image plates read with a Fujifilm BAS 1800-II bioimaging analyzer. The XRD data were calibrated using a calcite (CaCO₃) standard and the unit cell parameters were refined using the CelRef module of the LMGP package.^[23]

2.6. *Transmission electron microscopy (TEM) and electron diffraction (ED)*

Drops of dilute crystal suspensions were deposited onto glow-discharged carbon-coated grids and allowed to dry. The specimens were observed under low dose illumination with a Philips CM200 'Cryo' microscope operating at 200 kV. For electron diffraction, the TEM grids were mounted on a Gatan 626 specimen holder and fast-frozen into liquid nitrogen prior to being introduced in the microscope. The specimens were observed at low temperature (-180 °C) and base-plane ED patterns were recorded from selected areas of about 1 μm^2 . Images and diffraction patterns were recorded on a TVIPS TemCam F216 camera. The ED patterns were calibrated using a gold-coated carbon film as standard.

2.7. *Molecular modeling*

Left- and right-handed amylose helices having 6, 7, or 8 glucosyl units per turn and the hydroxymethyl groups in gauche-gauche (gg) conformation were generated by propagating a α -D-glucosyl residue in ⁴C₁ chair conformation. The glucosyl residues were taken from the previously reported rigid helices.^[14] The energy of the resulting helices was not further optimized. The non-bonded interaction was considered using Buckingham's potential.^[24] This function was applied with a cutoff of 1 nm. The molecule geometry was optimized using the

Universal Force Field^[25] in the Forcite module of Materials Studio.^[26] The molecular models were drawn with the Mercury software.^[27]

3. Results and discussion

3.1. Morphology and crystal structure as a function of the complexing agent

The complexes prepared with our series of bicyclic compounds were divided into two classes according to their morphology and diffraction patterns in the hydrated state. As shown in **Figure 2a-d**, the crystals formed in the presence of BORN, CAMP, DNAP and CDNAP are more or less hexagonal stacks of hexagonal unit lamellae, favored by dislocation-induced spiral growth. The base-plane ED patterns recorded from frozen-hydrated crystals exhibit a hexagonal symmetry and resemble those recorded from V_{6I} complexes prepared with ethanol^[10] or fatty acids.^[22] They are all similar to that of V_{BORN} shown as an example in **Figure 2e**. However, although the V_{6I} crystals are also hexagonal, the ED pattern is homothetical and can be indexed using a hexagonal unit cell with average parameters $a = b = 1.51 \pm 0.02$ nm which are larger than those of V_{6I}. These values are in good agreement with those calculated from the XRD powder patterns ($a = b = 1.53 \pm 0.01$ nm and $c = 0.81$ nm) (**Figure 2f**). Assuming a close-packed structure, the unit cell parameter would thus correspond to the diameter of one amylose helix consistent with a 7-fold conformation.^[4,17] However, as previously mentioned by Zaslav,^[17] 7-fold helices cannot be packed into a true crystallographic hexagonal unit cell. Consequently, a pseudo-hexagonal orthorhombic unit cell must be used to describe the crystal structure, with parameters $a = 1.53 \pm 0.01$ nm, $b = a\sqrt{3} = 2.65 \pm 0.01$ nm and $c = 0.81$ nm. Consistent with the constraint of chain-folding, each unit cell would contain two antiparallel 7-fold helices. Due to the close-packed arrangement, the complexing agent is expected to be only located inside the helix while water molecules would be located in the narrow inter-helical space (**Figure 6**). To our knowledge, it is the first time that the formation of hexagonal V-amylose crystals corresponding to the close-packing of 7-fold helices is reported.

A different type of crystals was observed for complexes prepared with DNAP and CDNAP. They were rectangular monolamellae that generally grew in the form of dense flower-like aggregates (**Figure 3a,c**). When a recrystallization step was carried out as described in the Experimental Section, the crystals were more individualized (**Figure 3b,d**), facilitating the recording of a base-plane ED pattern. The pattern (**Figure 3e**) was indexed using a two-dimensional orthorhombic unit cell with $a = 2.83 \pm 0.01$ nm and $b = 2.97 \pm 0.01$ nm, in good agreement with the values calculated from XRD data ($a = 2.82 \pm 0.01$ nm, $b = 2.97 \pm 0.01$ nm)

(**Figure 3f**). The crystals prepared with BPIN and TDEC yielded similar XRD patterns. These unit cell parameters correspond to those of the V7 allomorph formed by crystallizing amylose with 2-propanol,^[4,14,28] *tert*-butanol, 2-methylpropan-1-ol,^[4] menthone, fenchone, geraniol^[29] and terpineol.^[30] Combining packing energy and crystallographic analyses, Nishiyama et al. proposed a molecular model for the unit cell of the V_{2-propanol} complex in which four antiparallel left-handed 7-fold helices are packed along the $P2_12_12_1$ symmetry.^[14] The 2-propanol molecules would be located both inside and between the helices, together with some water molecules. We thus assumed that it was also the case for the bicyclic complexing agents yielding the same allomorph.

To distinguish between the two allomorphs described above, and according to the proposal of Helbert to number the allomorphs according to increasing inter helical space,^[8,31] the new pseudo-hexagonal structure (hexagonal crystals) will be referred to as V7_I (**Figure 6e**) in the following and the already known orthorhombic allomorph (rectangular crystals) as V7_{II} (**Fig. 6f**).

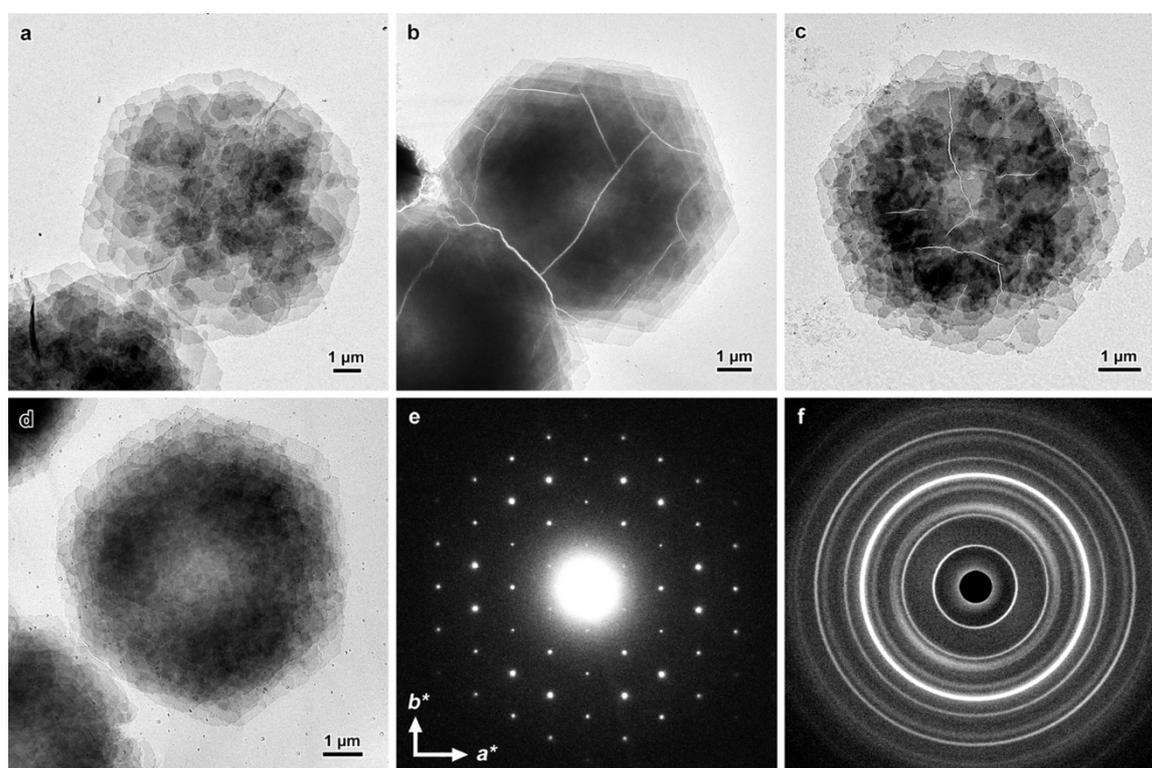


Figure 2. a-d) TEM images of V-amylose complexes prepared with CDNAP (a), DNAP (b), CAMP (c) and BORN (d). e) Base-plane ED pattern recorded at low temperature from a frozen-hydrated V_{BORN} crystal. f) XRD powder pattern recorded from hydrated V_{BORN} crystals.

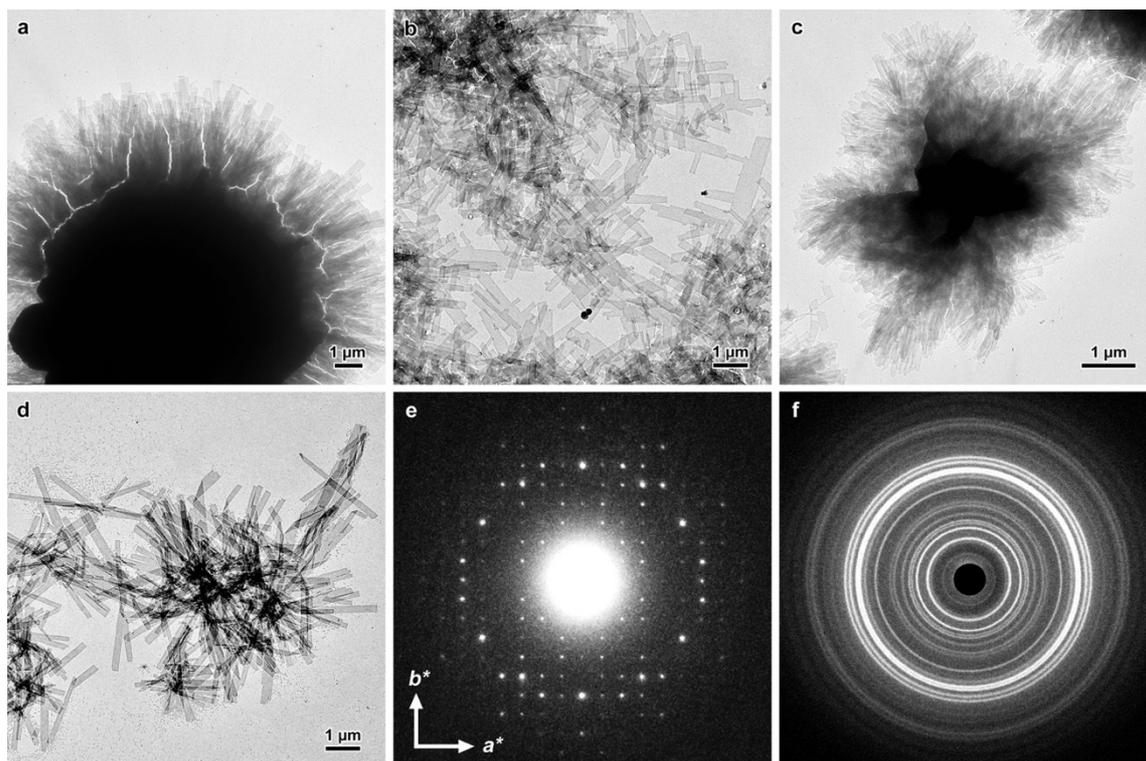


Figure 3. a-d) TEM images of V-amylose crystals prepared with DNAP (a,b) and CDNAP (c,d). Images "a" and "c" correspond to the first crystallization while those in "b" and "d" show more individual crystals after one recrystallization step. e) Base-plane ED pattern recorded at low temperature from a frozen-hydrated V_{CDNAP} crystal. f) XRD powder pattern recorded from hydrated V_{DNAP} crystals.

3.2. Effect of complexing agent and temperature on the complex formation

Table 1 shows the V-amylose allomorphs formed with our series of bicyclic compounds as a function of crystallization temperature. Within our range of crystallization conditions, all tested complexing agents induced V7 complexes, which is consistent with the molecular dimensions of the bicyclic compounds.^[32] However, this result disagrees with that reported by Helbert who observed the formation of V6_I with TDEC and BORN.^[8]

Since this is the first time that V7_I has been obtained with some bicyclic compounds (CDNAP, DNAP, CAMP, BORN), it seems that this allomorph is much less prevalent than the rectangular V7_{II} which has been prepared with a variety of complexing agents such as linear fatty acids,^[22] ketones,^[31] 2-propanol,^[28] branched alcohols,^[4] monoterpenes and many cyclic compounds.^[8,20,29,30,33] So far, the structural characteristics of the complexing agent that controls the allomorphic type of V-amylose remain unclear. Furthermore, a given complexing agent such as CDNAP and DNAP could induce both V7_I and V7_{II} in appropriate crystallization conditions.

The range of crystallization temperature was shown to vary with the complexing agent even when crystallization resulted in the same allomorph. For V7_I: $V_{\text{BORN}}, V_{\text{CAMP}} < V_{\text{CDNAP}} <$

V_{DNAP} ; for $V7_{\text{II}}$: $V_{\text{TDEC}}, V_{\text{BPIN}} < V_{\text{CDNAP}} < V_{\text{DNAP}}$ (**Table 1**). The result also suggests that the presence of a hydroxyl group (CDNAP, DNAP) allows the complexing agent to form crystalline V-amylose complexes at higher temperature compared to those having no functional group (BPIN, TDEC). For V_{CDNAP} and V_{DNAP} , $V7_{\text{I}}$ crystallized at higher temperatures than $V7_{\text{II}}$. This result is in agreement with the previous observation on V6 complexes that the more compact hexagonal $V6_{\text{I}}$ is favored at higher crystallization temperatures.^[22]

Table 1. Allomorphic type of the V-amylose complexes as a function of complexing agent and incubation temperature.

Complexing agent	Incubation temperature (°C)						
	25	40	50	60	75	100	115
TDEC	$V7_{\text{II}}$	$V7_{\text{II}}$	-	-	-	-	-
BPIN	$V7_{\text{II}}$	$V7_{\text{II}}$	-	-	-	-	-
CDNAP	$V7_{\text{II}}$	$V7_{\text{II}}$	$V7_{\text{II}}$	$V7_{\text{II}}$	$V7_{\text{II}}$	$V7_{\text{I}}, V7_{\text{II}}$	-
DNAP	$V7_{\text{II}}$	$V7_{\text{II}}$	$V7_{\text{II}}$	$V7_{\text{II}}$	$V7_{\text{II}}$	$V7_{\text{I}}, V7_{\text{II}}$	$V7_{\text{I}}, V7_{\text{II}}$
BORN	$V7_{\text{I}}$	$V7_{\text{I}}$	$V7_{\text{I}}$	$V7_{\text{I}}$	$V7_{\text{I}}$	-	-
CAMP	$V7_{\text{I}}$	$V7_{\text{I}}$	$V7_{\text{I}}$	$V7_{\text{I}}$	$V7_{\text{I}}$	-	-

3.3. Drying and rewetting

The XRD profiles of the two allomorphs of V_{DNAP} crystals in hydrated and dry states, and rewetted after vacuum-drying, are shown in **Figure 4**. Despite having different structures in the hydrated state, both allomorphs yielded almost identical XRD patterns after drying. A similar behavior was observed for V_{CDNAP} complexes. These patterns are similar to those obtained by drying the V7 complexes prepared with *tert*-butanol, 2-propanol,^[4,17] ketones^[34] and fatty acids.^[21] They can be indexed according to a pseudo-hexagonal orthorhombic unit cell with average parameters $a = 1.50 \pm 0.01$ nm and $b = a\sqrt{3} = 2.60 \pm 0.01$ nm. These unit cell parameters are slightly smaller than those of hydrated $V7_{\text{I}}$. This would result from a loss of water molecules located between the helices. By analogy with the $V6_{\text{a}}$ allomorph described in the literature (**Figure 6a**) and prepared by dehydrating $V6_{\text{I}}$ (**Figure 6b**),^[35] this anhydrous structure will be referred to as $V7_{\text{a}}$ in the following. In addition, the transition of the orthorhombic $V7_{\text{II}}$ (**Figure 6f**) to the pseudo-hexagonal $V7_{\text{a}}$ (**Figure 6d**) could be accounted for by a departure of interstitial ligands.

However, surprisingly, the parent V7_I and V7_{II} structures were completely recovered after rewetting the corresponding dry complexes (**Figure 4**), which suggests that the ligands were not extracted upon drying and the structural transition was only due to a loss of water molecules from the initial structures. In fact, a solid complexing agent such as CDNAP is unlikely to be released by the crystal upon drying. Therefore, the above results raise the questions of the location of the ligand in the interstitial space of V7_{II} crystals and the role of water in the structural recovery observed upon rehydration.

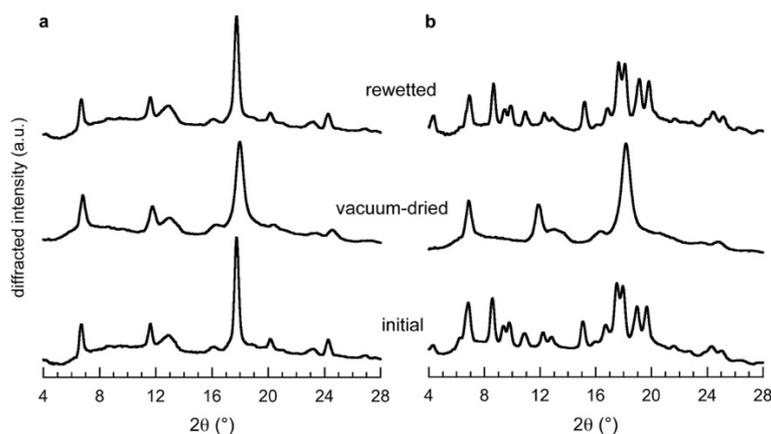


Figure 4. XRD profiles recorded from V_{DNAP} crystals in initial (hydrated), vacuum-dried and rewetted states: a) V7_I, b) V7_{II}.

3.4. Treatment with methanol

The XRD profiles in **Figure 5** illustrate the effect of washing V7_I and V7_{II} complexes prepared with DNAP with methanol before and after vacuum-drying. A general observation is that the characteristic reflections of the hydrated structures disappeared and that the crystallinity significantly decreased after the treatment with methanol. On the one hand, the XRD profile of V7_I washed with methanol and undried reveals a low crystallinity and the diffraction peaks are too broad to be properly indexed (**Figure 5a**). On the other hand, after the same treatment, V7_{II} crystals yielded the typical diffraction profile of the V6_{II} allomorph (**Figures 5c**), corresponding to an orthorhombic unit cell with $a = 2.66 \pm 0.01$ nm and $b = 2.72 \pm 0.01$ nm, and that was reported for complexes prepared with *n*-butanol and some fatty acids (**Figure 6c**).^[12,22] Upon vacuum-drying, both samples yielded identical well-defined diffraction profiles showing an increase in crystallinity (**Figures 5b,d**). These patterns are similar to those reported for the V6_a allomorph,^[32] corresponding to a pseudo-hexagonal orthorhombic unit cell with $a = 1.30 \pm 0.01$ nm and $b = 2.25 \pm 0.01$ nm (**Figure 6a**). A similar behavior was observed for V7_I complexes prepared with CAMP and BORN.^[31] This result is in good agreement with previous reports on

other V7_{II} complexes.^[32,34] The transition from the 7-fold to the 6-fold helical conformation of amylose would be due, on the one hand, to the extraction of the bicyclic compounds by methanol in which they are soluble and, on the other hand, to their possible exchange with the smaller methanol molecules. This result would thus reveal the crucial role of the complexing agent on the stability of the helical conformation.

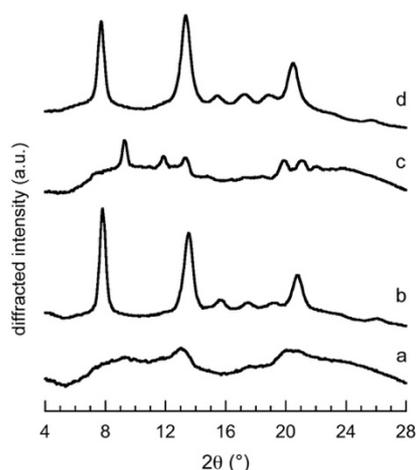


Figure 5. XRD profiles of V_{DNAP} crystals: V7_I washed with methanol and kept solvated (a), and dried in vacuum (b), V7_{II} washed with methanol and kept solvated (c), and dried in vacuum (d).

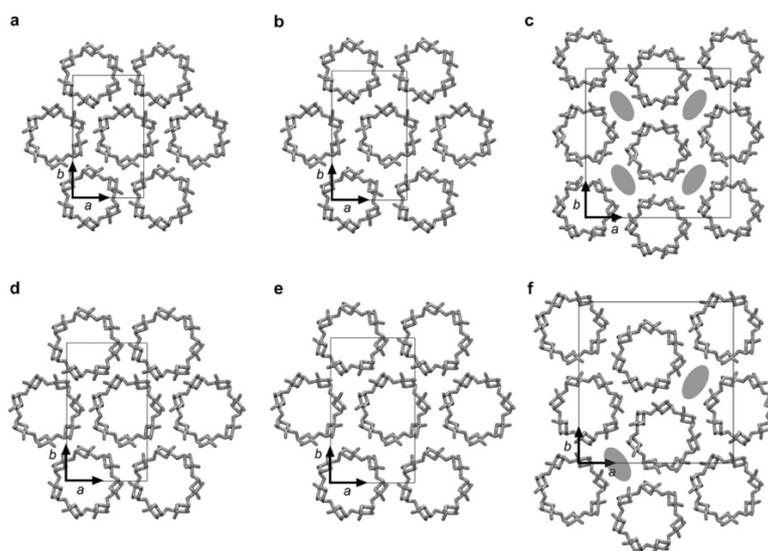


Figure 6. Molecular models of the six allomorphs of V-amylose considered in this study: a) V6_a, b) V6_I, c) V6_{II}, d) V7_a, e) V7_I, f) V7_{II}. The helix packings in a, b, c and f are those proposed for V_a,^[35] V_h,^[10] V_{*n*-butanol}^[12] and V_{2-propanol},^[14] respectively. In these base-plane projections along the helical *c*-axis, only the amylose helices have been drawn. Hydrogen atoms have been omitted for clarity. The conformation of the hydroxymethyl group has been fixed as *gg* in all cases for simplicity and the helices were kept undistorted. The gray ovals mark the inter-helical cavities. The unit cells have been superimposed on the models. Pseudo-hexagonal orthorhombic unit cells have been used in a, b, d and e.

4. Conclusion

In this study, several bicyclic compounds were used to induce the formation of crystalline complexes of amylose. All of them induced 7-fold amylose helical conformations but the packing arrangement varied depending on the complexing agent. BORN and CAMP yielded the new compact pseudo-hexagonal V7_I while TDEC and BPIN produced the orthorhombic V7_{II}. CDNAP and DNAP induced the formation of both allomorphs, V7_I being favored at higher crystallization temperatures than V7_{II}. Water was shown to play a crucial role in the packing arrangement and stability of the amylose helices. On the one hand, upon vacuum drying, both V7_I and V7_{II} allomorphs converted into the anhydrous hexagonal V7_a but the initial structures were recovered by rewetting the crystals in water at room temperature. On the other hand, washing the crystals with methanol followed by vacuum-drying resulted in the transition from 7-fold to 6-fold helices, highlighting the significant role of the complexing agent on the stability of the amylose conformation. Further work is in progress to determine more precise molecular models from packing analyses and crystallographic data, and shed some light on the location and orientation of the guest molecules as a function of the crystallization conditions of V-amylose.

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